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Optimization of Low Temperature Vitrification for Surface Analysis of Hydrated Hydrogel Polymers

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ABSTRACT

A method for analyzing hydrated hydrogel polymer surfaces in ultra-high vacuum atmospheres has been developed. The materials used for this study were commercially available poly(2-hydroxyethylmethacrylate) (HEMA) based hydrogel polymer ("soft") contact lenses. Application of a temperature controlled sample handling attachment for maintaining liquid nitrogen temperature samples is discussed. Issues such as sample handling, sample preparation, X-ray damage, temperature, contaminants in the samples and hydrocarbon contamination from the vacuum system have been investigated and controlled. Compared to a hydrated surface, specific surface enrichments of various components such as poly(dimethylsiloxane) and poly(N-vinylpyrrolidone) on the dehydrated surface are detected. This is likely due to surface energetics and differences in hydrophobicity/hydrophilicity of the components.

I. INTRODUCTION

The present study involves the development of methods to overcome the experimental difficulties of analyzing the hydrated surface of a hydrogel polymer during ultra-high vacuum (UHV) spectroscopic analysis. As a class of polymeric materials, hydrogels pose unique, interesting and challenging questions for ultra-high vacuum surface science. They are unique in that they are a polymer network that can absorb a proportionately large amount of water (swelling) without dissolving. Further, the properties of hydrogels undergo radical change between wet and dry states. For example, they are rigid when dry, and are pliable when wet.[1]

The wet state of the hydrogel system is not only incompatible with vacuum, but the resulting dehydration would be detrimental to the vacuum system. Thus, studies of wet hydrogel surfaces by ultra-high vacuum techniques (e.g. Electron Spectroscopy for Chemical Analysis (ESCA), Secondary Ion Mass Spectrometry (SIMS)) are not possible without utilizing a special sample handling technique-- a controlled temperature sample handling probe. A wet hydrogel can be frozen in liquid nitrogen, loaded onto the cooled stage attachment (generally, the temperature should be below the glass transition temperatures (T_g) of the polymers that form the hydrogel, typically below

-120°C) and the surface is maintained in its hydrated state in vacuum. This state is referred to as a "vitreous" state. By keeping the surface frozen, during exposure to the vacuum of the experimental chamber, a hydrated state surface is preserved as "wet". Since the sample is not pumped completely dry (some sublimation occurs during sample evacuation), the vacuum chamber does not suffer the harmful effects of desorbed water.[2] Warming the sample to room temperature and allowing any residual water trapped in the matrix to pump off (in a preparation chamber) will provide a dry dehydrated surface for analysis.

An important question is whether such a frozen vitrified surface in vacuum is equivalent chemically and thermodynamically to a hydrated surface at room temperature. While this is a question that is currently impossible to address for ultra-high vacuum analysis, it is believed that the frozen state surface is at least a useful representation of a room temperature hydrated hydrogel surface, especially given the information available from ESCA and SIMS (e.g. composition). Therefore, techniques utilizing the low temperature sample stage allow for the analysis of the differences between hydrated and dehydrated hydrogel surfaces.

There has been little published surface analytical work done on hydrated hydrogel materials because of the difficult sample handling requirements mentioned above. Most contact lens hydrogel material is based on the polymer poly(hydroxyethyl methacrylate) (HEMA) and HEMA based materials have been previously studied.[3] One published report involved analysis of hydrogel surfaces by Scanning Electron Microscopy (SEM). This work addresses the question of topography and roughness of the HEMA surface in wet and dry states by using a temperature control stage on a scanning electron microscope.[4] While the results of this preliminary study were inconclusive with respect to determining the gel structure, useful information about sample handling was obtained,

namely that using a temperature controlled stage is a more reliable method for obtaining an image of the hydrated gel structure[4]. A previous low temperature ESCA study of radiation grafted hydrogel materials on various polymer substrates has been reported[5,6]. For HEMA grafted on medical grade poly(dimethylsiloxane) (DMS), the results showed that, when frozen, the HEMA graft was at the outermost surface of the substrate. As the surface was dehydrated, the DMS became the dominant species at the surface, indicating the HEMA chains were burying themselves in the substrate.[5,6] This result is useful for the present work since some of the samples analyzed contain DMS embedded in a HEMA network, which show similiar segregation effects as in the grafted case (HEMA at the hydrated surface, DMS at the dehydrated surface).

In the present study, we report ESCA data from frozen (vitreous) and dehydrated surfaces of commercial contact lenses based on poly(2-hydroxyethylmethacrylate) (HEMA) hydrogels (Bausch & Lomb's Optima Toric, Bausch & Lomb SeeQuence, Johnson & Johnson Acuvue, and CIBA Vision NewVue lenses). Surface elemental and chemical data are reported.

If one is to study a hydrated surface with an UHV technique, four important experimental concerns must be addressed at the outset of the study to ensure reliable, accurate data. They are:

A. X-Ray damage (for ESCA) or ion beam damage (for SIMS) of the sample due to the analysis conditions must be limited.

B. The temperature necessary to obtain and maintain a hydrated state vitreous sample must be controlled and kept below the lowest glass transition temperature of the components of the sample (in this case below -120°C).

C. The effects of additives to the polymer, additives from storage in saline, such as salt ions, and impurities must be understood.

D. Pump oil contamination, a possibility due to condensation caused by the low temperatures used for analysis, must be eliminated or minimized.

The x-ray source on the ESCA instrument used in this work is not monochromatic. Stray secondary electrons from the source can impinge on the sample and can degrade polymer surfaces[1,2]. Additionally, sample heating can occur, thereby destroying the "vitreous" state, which leads to the concern for temperature control.

II. EXPERIMENTAL

A. Materials

Bausch & Lomb's SeeQuence and Optima Toric, Johnson & Johnson's Acuvue, and CIBA Vision's NewVues soft contact lens samples were obtained as received in commercial packages. The compositions of the lenses are shown in Table I. The lenses were analyzed "as received" from their packaging and after a salt ion extraction wash. Salt ions from the saline storage solutions were extracted from the contact lenses by immersing them in an ultrasound bath of 25 ml of triply distilled water for 10 minutes, pouring off most of the water, refilling to 25 ml and sonicating for 10 more minutes. This procedure satisfactorily removed salt ions to a concentration that was at the limit of detection of ESCA, and hence were not interfering in the analysis. The reasons for the washing procedure are outlined in the results section.

Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP, Teflon) (Dupont, Wilmington, DE) samples were used to test the hydrocarbon contamination levels caused by the sample handling protocol. Pieces were cut to the size of the sample stage, and cleaned in ultrasonic baths of hexane followed by methanol[7]. These samples were analyzed using the fully refined sample handling

technique as a final test of the method.

Different sample preparations were used as the method was being developed. The data presented for the x-ray damage, effect of temperature and effect of salt ions sections used the following method. Hydrated samples were prepared by mounting them (from solution) on an ESCA stage, adding a drop of triply distilled water to the surface, then immersing the stage in a Dewar vessel of liquid nitrogen for about three minutes. The stage was held on a stainless steel fork and slowly lowered into the liquid nitrogen. The sample was considered frozen when the liquid nitrogen reached a smooth boil around the stage. The lens itself was not immersed in liquid nitrogen as it fragments due to thermal shock. Once the sample was frozen, it was loaded onto the side arm (Figure 1) and pumped down to a vacuum of $1x10^{-3}$ torr for about two minutes. There was no nitrogen purge in the cross and no foreline trap present for these samples. The frozen sample was then transferred to the heatable/coolable sample holder, which had been evacuated to ultra-high vacuum and pre-chilled to approximately -130°C. Liquid nitrogen was pumped through the rod to achieve the base temperature of about -130°C before sample loading. (The prechamber that houses the rod must be evacuated to attain this low temperature as the rod relies on vacuum to insulate it from the warm external atmosphere). Vitreous samples were maintained by keeping the temperature of the rod and sample at or below -120°C. An indication that the sample was ready for analysis was the disappearance of the frost that formed on the stage during loading. Generally, the sample was retained on the heatable/coolable sample holder for at least four hours while subliming the frost off the rod and pumping down to ultra-high vacuum. Dehydrated samples were obtained by allowing the rod to warm up to room temperature while still under vacuum.

The data shown for the hydrocarbon contamination section followed the same freezing protocol

with refinements. These samples were prepared for hydrated (vitreous) state analysis by loading them wet on the sample stage, passing them through the side arm cross that was being purged by nitrogen to displace any water or other gaseous contaminants, and immersing them in liquid nitrogen. Once frozen, the sample was lifted through the cross to the side arm fork, loaded, the vacuum pump connected, the cross sealed, the nitrogen purge shut off, and the roughing pump valve opened to begin pumping with the roughing pump with the foreline trap in place (see Figure 1). After about one minute the sample was transferred to the pre-chilled sample manipulator (cooled to -140 C or below) to pump the sample down to ultra-high vacuum for analysis. As described above, the samples sat on the rod for at least four hours in the preparatory chamber to ensure a low operating pressure (5×10^{-8} torr or below) in the main chamber upon the subsequent sample transfer. The dehydrated states for the hydrocarbon contamination study samples were also obtained by allowing the hydrated sample to warm up to room temperature under vacuum on the heatable/coolable rod.

This sample handling method differs from the previously published protocol[5] in that the samples are always held at -120°C or colder. No sublimation step or intermediate freezing step under vacuum was performed as was done in the referenced work[5]. The protocol reported here involves freezing the sample to its vitreous state (-120° C or colder) under an atmospheric pressure nitrogen purge, then sample evacuation to ultra-high vacuum conditions during which the vitreous temperature is maintained.

B. ESCA Instrumentation

The ESCA spectra were collected using a Perkin-Elmer Physical Electronics Model PHI 5100 ESCA. This instrument employed a hemispherical analyzer with a single channel channeltron electron multiplier detector. Mg Kα X-rays (1253.6 eV) from a dual anode source were used as an nonmonochromatized source operated at 300 W, 15 kV, and 20 mA. The base pressure of the system was $5x10^{-10}$ torr with an operating pressure typically $1x10^{-7}$ torr. Pass energies of 178.95 eV for survey spectra, and 71.55 eV for elemental multiplex spectra were used. Spectra were taken at a 45° take-off angle. The spectrometer had been modified to handle vitreous samples through the use of a special sample handling stage system and is shown on Figures 1A,B. The regular eight position sample carousel was removed and a single sample stage rod was bolted in its place.

C. The Heatable/Coolable Sample Probe

The sample rod was purchased from U.H.V. Instruments, Niagara Falls, NY (U.H.V. now does business as Advanced Plasma Systems, Mississauga, Ontario, Canada). The apparatus, shown on Figures 1A and 1B, consists of a side arm, onto which the sample stage was loaded and pumped down to rough vacuum pressure (10 mtorr) by a rotory pump. The arm carries the sample into the introduction chamber that housed the heatable/coolable arm of the appartaus. A Kurt J. Lesker (Clairton, PA) model number MMA-102-2QF Micromaze foreline trap was mounted at the head of the roughing pump (see Figures 1A,B) to eliminate backstreaming oil mist contamination. The second arm, the arm of the heatable/coolable probe held the sample stage on the hot/cold block. The side arm was retracted and the heatable/coolable rod was used to maintain the sample temperature

at or below -120°C during sample pumpdown and analysis.

The heatable/coolable arm consists of a claw that can be opened and closed for sample loading, holding, and unloading, a liquid nitrogen cooling line, and an xyz manipulator for sample introduction into the main chamber and alignment for analysis.

There are two methods used to cool the heatable/coolable rod. The first method used a Welch Duo-Seal 1397 roughing pump to pull liquid nitrogen from a Dewar through the cooling lines. The liquid nitrogen was pumped through the rod to achieve the base temperature of about -120°C before sample loading.

The second method relies on forcing liquid nitrogen through the cooling lines. To perform this operation, a twenty foot length of quarter inch copper tubing was formed into a condensation coil. The coil was connected to the probe on one end and to a tank of nitrogen (99.995%, AGA Gas, Inc., Cleveland, OH) on the other end. The condenser coil was placed in a Dewar vessel of liquid nitrogen. The gaseous nitrogen was cooled and condensed to liquid nitrogen in the copper condenser immersed in liquid nitrogen. The gas flow forced the liquid nitrogen through the cooling lines on the probe to cool the rod. (Extreme caution must be used when the experiment is over and the condenser is removed from the liquid nitrogen. The liquid nitrogen formed in the condenser expands rapidly to a gas if the coil is warmed too quickly. Therefore, it is suggested that the coil be disconnected from the nitrogen tank before the coil is slowly raised from the Dewar vessel to allow the liquid room to expand to a gas. Not following this precaution can cause an explosion.)

The prechamber that houses the rod must be evacuated to attain the low temperatures required for analysis since the rod relies on vacuum to insulate it from the external atmosphere. Vitreous samples were maintained by keeping the temperature of the rod and sample at or below

-120°C. Generally, the sample sat on the heatable/coolable rod for at least four hours while evacuating to ultra-high vacuum. Once the introduction chamber was evacuated to ultra-high vacuum, the side arm was used to position the sample under the X-ray in the main chamber for analysis via the xyz manipulator.

III. RESULTS AND DISCUSSION

A. X-Ray Damage Study

The x-ray source on the ESCA instrument employed is not monochromatic. Stray secondary electrons from the source can impinge on the sample and cause degradation of polymer surfaces[1,2]. An experiment was developed to evaluate x-ray damage to the lens during analysis. A Johnson & Johnson Acuvue lens was loaded and analyzed for x-ray damage. The base polymer of this material is a blend of 98% HEMA, and 2% poly(methacrylic acid) homopolymers. The sample was not vitreous as the temperature rose above -120°C during the analysis. The carbon 1s spectra in Figure 2 demonstrated the chemical changes in the lens with x-ray exposure time. Figure 2A displays a carbon 1s spectrum after 40 minutes under the x-ray. The envelope resembles that expected from dry HEMA. After eighty total minutes of x-ray source exposure, the spectrum in Figure 2B resulted. This carbon 1s envelope was beginning to show a change indicating x-ray damage. A shoulder at lower binding energy than the CH_x peak appeared at 285 eV and the once resolved CH_x and C-O bands are now one broad peak. A concomitant loss of elemental oxygen and the loss in C-O functionality at the surface are consistent with graphitization. Figure 2C shows the spectrum after 120 minutes of x-ray exposure. The carbon 1s envelope no longer resembled a HEMA spectrum (Figure 2A) but appeared as a single, graphitic carbon peak.

The elemental composition (expressed as atomic concentration percentages) in Table II demonstrate the surface damage due to these analysis conditions. After 40 minutes of analysis time, the carbon and oxygen percentages of 60.7 and 24.3 roughly approximated the percentage of carbon and oxygen in HEMA. There are 3 oxygens to 6 carbons in HEMA's structure, a 2:1 ratio. The discrepancy could be due to some loss of oxygen due to damage, signal attenuation from salt or impurity in the lens. After 120 minutes of x-ray exposure, the carbon percentage increased to 86.2% and the oxygen concentration is reduced to 9.0%. The loss of oxygen and increase in carbon content of the surface suggested that the lens material was destroyed in 120 minutes. Additionally, the sample had a yellow-brown spot in the center where the analysis was performed indicating damage.

For further work, spectra of the contact lenses were obtained in 30 minutes to minimize sample damage. If a second spectrum was desired or a wet/ dry analysis was performed on the same lens, the second spectrum was taken at another spot on the sample.

B. Temperature Study

The importance of temperature during the experiment was studied and the results are displayed in Figure 3 A,B,C and Table III. Dubochet[8] has shown the conditions for vitrification of ice and aqueous solutions. A vitreous sample can be described as a sample that has its hydrated molecular architecture frozen three dimensionally in place and retained while the water of hydration may be absent. This requires a temperature lower than the lowest T_g of the polymer constituents. The T_g of DMS is typically -120°C, so this threshold temperature was chosen. For the samples in this study, the contact lens surface is likely devoid of water, which has sublimed off in vacuum, but the molecular composition of the hydrated state should be preserved. Hydrated Johnson & Johnson

Acuvue lenses were analyzed for the temperature test. Figure 3A shows the carbon 1s envelope for an Acuvue lens at -121°C, and consisted of signals from $\underline{C}H_x$ band and an acid functionality (O-$\underline{C}$=O). Figure 3B is the carbon 1s envelope for a lens at -40°C. Figure 3C is a lens at +28°C. Note that the +28°C sample resembled a spectrum of dry HEMA. The spectra obtained at -40°C resembled the dehydrated state specimen, unlike the hydrated state. This indicated that the vitreous state was not preserved at this temperature despite the temperature being significantly lower than the freezing point of water.

Table III reports the elemental composition for samples at these three temperatures. According to the data, the lens analyzed at -40°C was within experimental error limits of the lens analyzed at +28°C. The slight difference in atomic percentages were most likely due to the minor elements of the salt ion affecting the analysis. (This effect is discussed below.) The results from the sample held at -121°C were dramatically different than those from the +28 and -40°C samples. This is interpreted as the differences between hydrated and dehydrated states. The -121°C temperature was required to preserve composition characteristic of the hydrated surface. For all results reported as "hydrated", specimens were kept at or below the -120°C mark to ensure the hydrated state was present as vitreous in nature. Dehydrated samples were analyzed at room temperature (approximately +28°C).

C. Effects of salt ions from saline storage solution

The third experiment investigated the effect of salt ions from the buffered saline storage solution. Salt ions in the lens material could potentially affect the analysis of the samples in two ways. Foremost is the calculation of elemental composition which can be altered. Secondly, the signal

from the polymer surface could be attenuated by deposited salts. Table IVa contains data obtained from hydrated CIBA Vision lenses. The base polymer for this lens is a HEMA-NVP copolymer. The first two sets of data are elemental concentrations for a lens with the salts present , i.e. with no extraction. The chlorine percentage was inflated by overestimation of the peak area of the chlorine 2s peak. This photoelectron peak had a carbon 1s satellite peak overlapping it[11]. Instead of stoichiometric NaCl, one obtains 5.2% Na, and 20.0% Cl. This effect can be corrected by using the chlorine 2p peak which does not have a satellite interference. The oxygen and carbon percentages are lower than expected and were in fact underestimated due to the salt ions included in the calculation. The "Salt present (b)" sample in Table IVa is for the same sample as in (a), but the intensities due to sodium and chlorine were excluded from the calculation. The carbon, oxygen and nitrogen percentages increased to values closer to those one would expect for this base polymer. The third, (c), line of the table contains the atomic concentration for a sample which was extracted by the procedure described in the experimental section. The concentrations of elements of the salt ions diminished to within error limits of zero, and the carbon, oxygen, and nitrogen percentages were within error limits equivalent to values expected for this type of material.

The saline related elements on the surface can disrupt the analysis by physically attenuating the polymer signal by forming a layer of salt crystals on the surface. Table IVb contains the data obtained from Bausch & Lomb Optima Toric lenses. In the process of dehydrating the polymer, the atomic percentages more than double from 2.4% to 5.3% for the NaCl ion elements. Further, the carbon atomic concentration was constant, while the oxygen level decreased 4.5% and the silicon percentage dropped from 3.8% to 2.8%. These observations suggested that the salt ions, trapped in the bulk polymer network in the hydrated state, followed the water out of the polymer network and

crystallized at the surface. This would explain the increase in elements due to saline buffer at the surface in the dehydrated state.

Evidence for this thesis can be obtained by examining the signal intensity from a prominant contaminant, the DMS. The solidified salts likely attenuated the signal from the polymer matrix, as evidenced by the decreased silicon levels. Thermodynamics dictate that the DMS should have been at the surface when dehydrated, and away from the surface when the lens was hydrated. If the DMS was supposed to be at the surface when dehydrated, the silicon concentration should increase, not decrease as it did in the sample with the salt ions. Extracting the salt ions in triply distilled water eliminated the attenuation effect. The third and fourth lines of Table IVb are of hydrated and dehydrated lens surfaces after the salts had been washed out. Note now that the silicon percentage increased dramatically at the surface upon dehydration. Since the silicon concentration originated from a contaminant, it was not present at the same concentration from lens to lens. This would explain why both silicon percentages are lower in the salt wash sample. The DMS was probably not being washed out of the lens by the washing protocol as DMS is hydrophobic. Extracting the salt ions out of the lens material removed the calculation error and the signal masking error, and allowed for more direct analysis of the base hydrogel materials in hydrated and dehydrated states.

D. Condensed hydrocarbon contamination

As noted in the experimental section, a foreline trap was mounted on the mechanical roughing pump used to evacuate the side arm that takes the sample into the cold probe. The trap should decrease or eliminate hydrocarbon contamination from backstreaming pump oil which condenses on the frozen sample. The atomic concentration data in Tables V, VI, and VII demonstrate an

improvement in vitreous sample preparation methodology as a result of using the foreline trap. The "old method" consisted of freezing the sample in liquid nitrogen in air, loading on the side arm fork, pumping to rough vacuum (1 minute) then transferring the sample to the cold probe which was pre-cooled to -140 C or below. In the brief time the frozen sample was in air, it condensed water as frost and organic contaminants. Table V contains data obtained using the "old method". This sample handling technique results in data that is not reproducible from sample to sample (JNJ A and B) or even spot to spot on the same sample (CIBA A and B). While one can get results that show the correct trend, they may not be accurate. CIBA samples C (wet) and C (dry) demonstrate that a change from the vitreous state (hydrated surface) to a dehydrated state can be observed. The nitrogen (from N-vinylpyrrolidone (NVP)) and silicon (from poly(dimethylsiloxane) (DMS)) atomic concentrations increase from hydrated to dehydrated state, which is expected based on surface energetics and hydrophilicity considerations. However, the atomic concentration values may not be accurate. CIBA sample D is a dehydrated sample that was dried by rough vacuum after the salt ions were washed from the lens. The sample was not frozen in liquid nitrogen. The atomic concentrations for this lens have higher values for silicon and nitrogen, suggesting that CIBA C (dry) is the dehyrated state surface that has hydrocarbon contamination left on the surface as a result of freezing the sample, attenuating the contact lens signals.

In an attempt to reduce contamination from freezing the lenses in air, the samples were frozen under a nitrogen gas purge. Data from this sample handling technique is shown on Table VI. This technique did little to improve the data. The three CIBA and two SeeQuence hydrated samples are not reproducible from sample to sample, and the Optima Toric sample has low oxygen content suggesting organic contamination. Figure 4 is the carbon 1s envelope for the hydrated Optima Toric

lens. Notice that the low binding energy hydrocarbon peak is very intense and the ester band (which is shifted on the spectrum shown to 289.5eV due to sample charging) is weak. The carbon 1s envelope for the dehydrated Optima Toric lens is shown in Figure 5. Note in this spectrum that the ester band is more prominant and a shoulder at 286.5 eV is discernable, due to the C-O of the HEMA alcohol functional group. This suggests that the hydrated surface is covered by a hydrocarbon contaminant, that does not have oxygen, and is attenuating the base polymer signal. It should also be noted that the dehydrated sample may still has some contamination, since the oxygen level is lower than one would expect for this sample.

The final refinement of the technique was the addition of a foreline trap on the roughing pump that pumps the side arm down to rough vacuum before transferring the sample to the cold probe. The hydrocarbon contamination discussed above is most likely condensed roughing pump oil on the lens surface. The foreline trap is designed to eliminate backstreaming oil vapors from the pump into the vacuuum. Table VII shows the results from the samples run with this filter in place.

These samples were prepared for hydrated (vitreous) state analysis by loading them wet on the sample stage, passing them through the side arm cross that was being purged by nitrogen to displace any water or other gaseous contaminants, and immersed in liquid nitrogen. Once frozen, the sample was lifted through the cross to the side arm fork, loaded, the vacuum pump connected, the cross sealed, the nitrogen purge shut off, and the roughing pump valve opened to begin pumping with the roughing pump with the foreline trap in place. After about one minute the sample was transferred to the pre-chilled cold probe (cooled to -140 C or below) to pump the sample down to ultra-high vacuum for analysis.

E. Comparision of sample handling methods

Results for samples prepared using the fully refined method are shown on Table VIII and representative carbon 1s spectra are shown in Figures 6A,B; 7A,B; and 8A,B. Note that for each lens line, the oxygen content has increased for the analysis of samples which are hydrated for this sample handling method compared to the data for the previous methods shown on Table VIII. Additionally, the carbon 1s spectra of the hydrated surfaces (see Figures 6A, 7A, and 8A) all have more prominant ester (O=C-O) bands approximately 3.5 eV higher binding energy than the intense CHx band than previously obtained (Figure 9 A,B,C). These observations suggest that the hydrocarbon contamination as a result of the freezing process has diminished.

The expected trends of increasing silicon and nitrogen concentrations are observed for the species presumed to migrate to the surface upon dehydration, namely the silicon levels from DMS, and the nitrogen levels from NVP. These compounds can be detected in the Optima Toric and the NewVues, although the DMS level in the NewVues appears to be lower. It should be noted that the data from the dehydrated NewVues are from a sample that was vacuum dried externally, without freezing. The reason for using an external drying method is the fact that the lenses often fragment upon warming to room temperature and drying. This is likely due to the lenses freezing with internal stress since they are mounted on the sample stage flat and try to assume the rounded shape they had initially. To eliminate this problem one must use a lens of high correcting power (which are thicker) or machine a rounded stage for mounting the sample in its cast molded, or lathed shape.

F. Hydrocarbon contamination test of fully refined method

To evaluate how much, if any, hydrocarbon contamination occurs on a frozen sample surface as a consequence of sample handling and evacuation to ultra-high vacuum, samples of FEP were analyzed following the sample handling protocol developed for vitreous sample handling. FEP has a low surface energy (18 to 20 dynes/cm)[9]. It was cleaned by a method that has been shown to result in a surface that is free of detectable hydrocarbon contamination[7]. FEP that had been ultrasonically cleaned in both hexane followed by methanol was analyzed after being mounted on a sample stage, frozen, and evacuated to ultra-high vacuum using the procedure developed for vitreous sample handling. If vapor phase or airborne hydrocarbons in the vacuum system were condensing on the frozen samples, it would be apparent on the FEP sample. There should be no interfering hydrocarbon peak in the carbon 1s spectrum of FEP, since all carbons are bound to carbon and fluorine[10]. Therefore, contamination would be evidenced by a low binding energy carbon peak 8.0 eV below the C-F band[7,10], and non-stoichiometric amounts of carbon and fluorine (as determined by analyzing a clean piece of FEP) reflected in the atomic concentrations (high in carbon, low in fluorine).

The results are shown on Table IX and Figure 10. The atomic concentrations for the frozen FEP sample suggest that there is less than 1% hydrocarbon contamination when compared to the room temperature sample. Figure 10, shows no low binding energy carbon indicative of hydrocarbon contamination. The peak observed is that of carbon bound to fluorine (the minor peak at 284.0 eV, 8.5 eV below the C-F band at 292.5 eV, is a Mg $K\alpha_3$ x-ray satellite line from the nonmonochromatized source employed)[11]. This result demonstrates that hydrocarbon contamination is not occurring during the process of freezing the sample, and evacuation to ultra-high vacuum.

Ratner has published data obtained on poly(tetrafluoroethylene) PTFE used to test his vitreous state sample handling method[6]. He speculates that during sample cool-down and vacuum evacuation, hydrocarbons deposit on top of a frozen water layer. These contaminants are "blown away"[6] during a sublimation step when ultra-high vacuum conditions are reached. The technique developed in this paper avoids this type of complication. The sample is rapidly frozen under nitrogen, in liquid nitrogen and maintained below the vitreous state temperature during evacuation to ultra-high vacuum conditions instead of undergoing a sublimation step during sample evacuation. The sublimation step previously reported holds the temperature of the sample at -40 to -80°C during sample evacuation on a stage that is being cooled on a cold probe arm. Additionally, the backstreaming trap removes the hydrocarbons from the atmosphere during evacuation. The results of the FEP test indicate that no condensation of hydrocarbons is occurring during sample analysis.

IV. CONCLUSION

Based on the data presented above, a sample handling protocol for analyzing hydrated polymer surfaces has been developed. The main steps involved can be summarized as:

1.) Precool the specimen rod to the desired analysis temperature, generally this is below -120° C.

2.) Backfill and purge the sample prechamber where the sample is to be frozen with a dry gas such as dry nitrogen to prevent the formation of frost and condensation of organic contamination.

3.) Freeze the sample in liquid nitrogen under the nitrogen purge.

4.) Evacuate the sample to rough vacuum pressure (10^{-3} torr) in an oil free environment.

5.) Load the sample onto the prechilled specimen rod and evacuate to ultra-high vacuum at or below the vitreous state temperature (again, usually -120° C).

6.) Analyze sample making certain sample damage and heating is not occurring during the analysis interval.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Bausch & Lomb, the National Science Foundation (NSF DMR 9303032), and the Office of Naval Research, Chemistry Division for funding this project.

REFERENCES

[1]D.T. Clark, in *Polymer Surfaces*, edited by D.T. Clark and W.J. Feast (John Wiley and Sons, New York, 1978), pp. 313, 321.

[2]D.R. Miller and N.A. Peppas, Macromolecules. **20**, 1258 (1987).

[3]B.D. Ratner, and A. S. Hoffman, in *Hydrogels for Medical and Related Applications*, edited by J. Andrade (American Chemical Society, Washington, DC, 1976), p.10.

[4]J. Andrade, R. King, and D. Gregonis, in *Hydrogels for Medical and Related Applications*, edited by J. Andrade, (American Chemical Society, Washington, DC,. 1976), pp. 206-213.

[5]B.D. Ratner, P.K. Weathersby, A.S. Hoffman, M.A. Kelly, M.A., and L.H. Scharpen, J. Appl. Poly. Sci. **22**, 643-664 (1978).

[6]B.D. Ratner, and D.G. Castner, Colloids and Surfaces B: Biointerfaces. **2**, 343-345 (1994).

[7]T.G. Vargo, P.M. Thompson, L.G. Gerenser, R.F. Valentini, P. Aebischer, D.J. Hook, and J.A. Gardella, Jr. Langmuir. **8**, 131 (1992).

[8]J. Dubochet, J. Lepault, R. Freeman, J.A. Berriman, J.-C. Homo, J. Microsc. **128**, 219-237 (1982).

[9]E.G. Shafrin, and W.A. Zisman, in *Contact Angle, Wettability, and Adhesion*, edited by R.F. Gould, (American Chemical Society, Washington, DC, 1964), p. 147.

[10]D.J. Hook, T.G. Vargo, J.A. Gardella, Jr., K.S. Litwiler, and F.V. Bright, Langmuir. **7**, 144 (1991).

[11]*Handbook of X-ray Photoelectron Spectroscopy*, edited by C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, and G.E. Muilenberg, (Perkin-Elmer Corp., EdenPrairie, MN, 1979), p. 13.

Table I: Contact Lens Polymer Compositions

Sample	FDA Tradename	Polymer Composition
Johnson & Johnson Acuvue	Etafilcon A	HEMA, MA homopolymers
CIBA Vision NewVues	Vifilcon A	HEMA-NVP copolymer
Bausch & Lomb Optima Toric	Hefilcon B	HEMA-NVP copolymer
Bausch & Lomb SeeQuence	None	HEMA homopolymer

HEMA-- poly(2-hydroxyethylmethacrylate)
MA-- poly(methacrylic acid)
NVP-- poly(N-vinylpyrrolidone)

Table II: X-Ray Damage Study--ESCA Atomic Concentrations for Acuvue Lenses

Sample State	C	O	Si	N	Na	Cl	(%)
40 min. dehydrated	60.7	24.3	0.0	0.2	8.2	6.6	
120 min. dehydrated	86.2	9.0	0.2	0.2	2.5	1.8	

(standard deviation ±0.3%)

Table III: Temperature Study--ESCA Atomic Concentrations for Acuvue Lenses

Sample State	C	O	Si	N	Na	Cl	(%)
-121°C	86.4	12.8	0.1	0.1	0.4	0.2	
-40°C	61.0	26.9	0.1	0.3	6.3	5.5	
+28°C	60.7	24.3	0.0	0.2	8.2	6.6	

(standard deviation ±0.3%)

Table IVa: Effects of Salt Ions, Calculation--
Atomic Concentrations of Hydrated NewVues Lenses

Sample State	C	O	Si	N	Na	Cl (%)
Salt present (a)	61.2	11.3	0.0	2.3	5.2	20.0
Salt present (b)	81.9	15.2	0.0	2.9	excluded	
Salt absent (c)	78.2	18.3	0.0	3.2	0.3	0.0

(standard deviation ±0.3%)

Table IVb: Effects of Salt Ions, Signal Masking--
Atomic Concentrations of Optima Toric Lenses

Sample State	C	O	Si	N	Na	Cl (%)
Hydrated + Salt	73.5	16.9	3.8	1.0	2.4	2.4
Dehydrated + Salt	73.0	12.4	2.8	1.2	5.3	5.3
Hydrated	79.0	19.2	0.6	1.2	0.0	0.0
Dehydrated	86.5	10.3	2.2	0.9	0.0	0.1

(standard deviation ±0.3%)

Table V: ESCA atomic concentration data obtained freezing the contact lens sample in air

Sample*	State**	C	O	Si	N (%)
J&J Acuvue--A	wet	87.9	12.1	0.0	0.0
J&J Acuvue--B	wet	90.0	9.1	0.0	0.0
CIBA NewVues--A	wet	89.3	10.6	0.0	0.1
CIBA NewVues--B	wet	84.3	19.6	0.0	0.1
CIBA NewVues--C	wet	82.2	17.7	0.0	0.1
CIBA NewVues--C	dry	82.9	14.2	0.2	2.7
CIBA NewVues--D	dry	76.2	17.5	0.6	5.8

(standard deviation ±0.3%)

* J&J is Johnson and Johnson, CIBA is CIBA Vision. The letter designation denotes an individual sample. The two CIBA NewVues--C samples means that the dry sample is the same lens used for the wet analysis.

** wet denotes the hydrated/vitreous state, dry denotes the dehydrated state.

Table VI: ESCA atomic concentration data obtained freezing the contact lens sample in a nitrogen purge

Sample*	State**	C	O	Si	N	(%)
B&L Optima T--A	wet	90.6	9.3	0.1	0.0	
B&L Optima T--A	dry	78.0	18.7	2.2	1.1	
CIBA NewVues--A	wet	82.2	17.7	0.2	0.0	
CIBA NewVues--B	wet	87.5	12.5	0.0	0.0	
CIBA NewVues--C	wet	85.8	14.2	0.0	0.0	

(standard deviation ±0.3%)

* CIBA is CIBA Vision , B&L is Bausch and Lomb, T is Toric. The letter designation denotes an individual sample.

** wet denotes the hydrated/vitreous state, dry denotes the dehydrated state.

Table VII: ESCA atomic concentration data obtained freezing the contact lens sample under nitrogen purge with a foreline trap on the mechanical vacuum pump.

Sample*	State**	C	O	Si	N	(%)
B&L Optima T--A	wet	82.3	16.0	1.1	0.6	
B&L Optima T--B	wet	85.3	13.5	1.2	0.0	
B&L Optima T--A	dry	72.2	24.3	2.1	1.4	
B&L Optima T--B	dry	73.0	21.0	4.8	1.2	
CIBA NewVues--A	wet	82.2	17.7	0.2	0.0	
CIBA NewVues--A	dry	(lens fragmented upon drying)				
CIBA NewVues--1	dry	76.2	17.5	0.6	5.8	
	(dried without freezing)					
J&J Acuvue--A	wet	81.7	18.1	0.0	0.2	
J&J Acuvue--A	dry	(lens fragmented upon drying)				
J&J Acuvue--1	dry	76.6	22.7	0.3	0.4	
	(dried without freezing)					
B&L SeeQuence--1	dry	77.0	22.4	0.4	0.2	
	(dried without freezing)					

(standard deviation ±0.3%)

* J&J is Johnson and Johnson, CIBA is CIBA Vision , B&L is Bausch and Lomb, T is Toric. The letter designation denotes an individual sample.

** wet denotes the hydrated/vitreous state, dry denotes the dehydrated state.

Table VIII: Comparision table of ESCA atomic concentration data obtained as the sample handling techinque was refined

Sample	State*	C	O	Si	N (%)
Frozen in air					
CIBA NewVues	wet	85.3	14.7	0.0	0.1
CIBA NewVues	dry	82.9	14.2	0.2	2.7
Frozen in nitrogen purge					
CIBA NewVues	wet	85.8	14.2	0.0	0.0
Frozen in nitrogen purge with foreline trap					
CIBA NewVues--A	wet	82.2	17.7	0.2	0.0
CIBA NewVues--1 (dried without freezing)	dry	76.2	17.5	0.6	5.8

(Standard deviation ±0.3%)

* wet denotes the hydrated/vitreous state, dry denotes the dehydrated state.

Table IX: ESCA atomic concentration data for frozen FEP

Sample	Carbon	Fluorine (%)
Frozen FEP	29.2	70.8
FEP	28.3	71.7

(standard deviation ±0.3%)

Figures and Figure Captions

Figure 1A: Diagram of cold probe, cooled by drawing liquid nitrogen through the cooling lines by vacuum

Figure 1B: Diagram of cold probe, cooled by forcing liquid nitrogen through the cooling lines under pressure

Figure 2: ESCA Damage Study-- Carbon 1s region obtained for a Johnson & Johnson Acuvue lens

A.) 40 minutes of X-ray exposure

B.) 80 minutes of X-ray exposure

C.) 120 miuntes of X-ray exposure

Figure 3: Effect of Temperature-- ESCA carbon 1s region for a Johnson & Johnson Acuvue lens

A.) -121°C

B.) -40°C

C.) +28°C

Figure 4: ESCA carbon 1s envelope for a hydrated Bausch & Lomb Optima Toric lens

Figure 5: ESCA carbon 1s envelope for a dehydrated Bausch & Lomb Optima Toric lens

Figure 6: ESCA carbon 1s envelope for a Bausch & Lomb Optima Toric lens using the fully developed sample handling method

A.) Hydrated state

B.) Dehydrated state

Figure 7: ESCA carbon 1s envelope for a CIBA NewVues lens using the fully developed sample handling method

A.) Hydrated state

B.) Dehydrated state

Figure 8: ESCA carbon 1s envelope for a Johnson & Johnson Acuvue lens using the fully developed sample handling method

A.) Hydrated state

B.) Dehydrated state

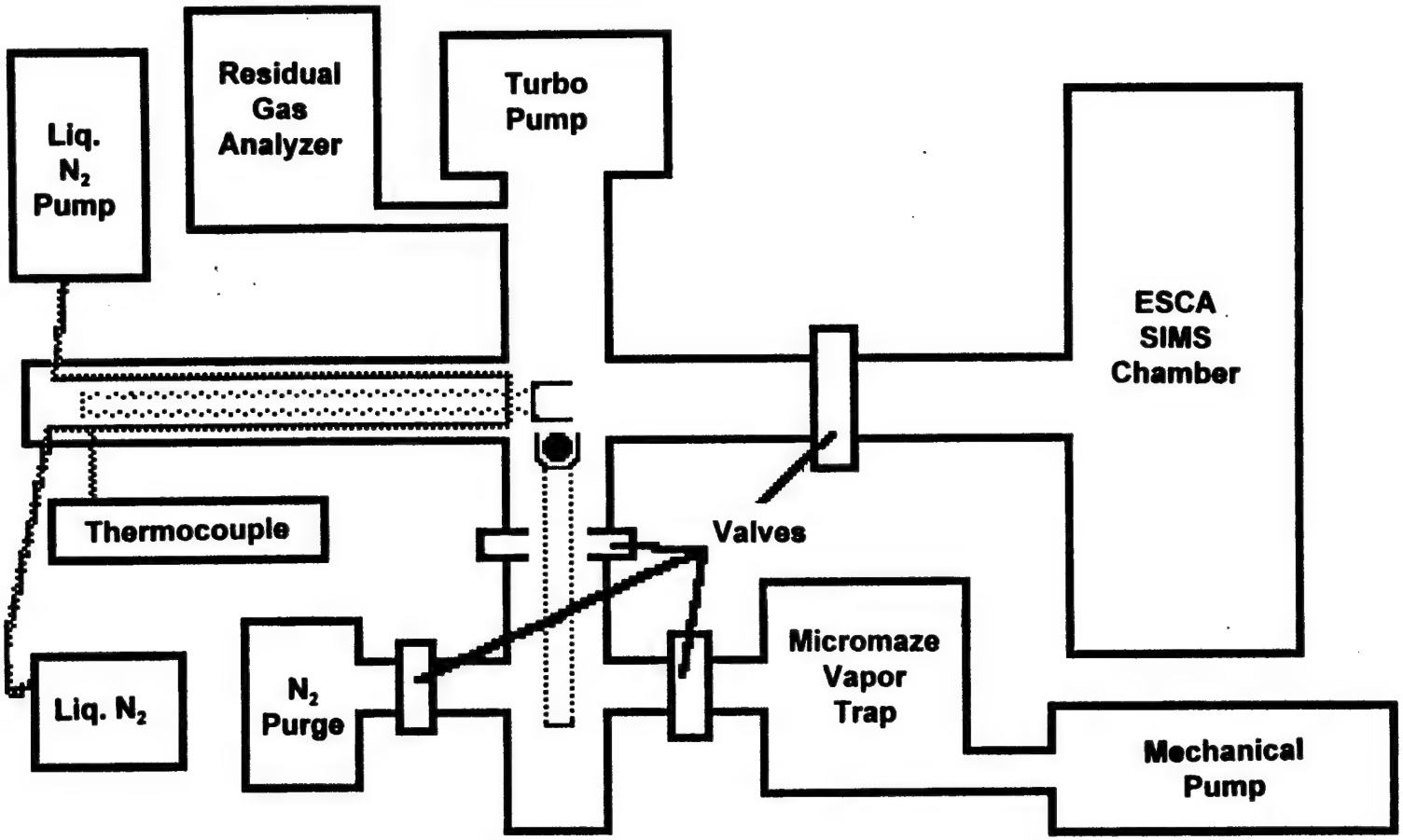
Figure 9: ESCA hydrated state carbon 1s envelopes without sample handling refinements

A.) Bausch & Lomb Optima Toric lens

B.) CIBA NewVues lens

C.) Johnson & Johnson Acuvue lens

Figure 10: Carbon 1s spectrum for frozen FEP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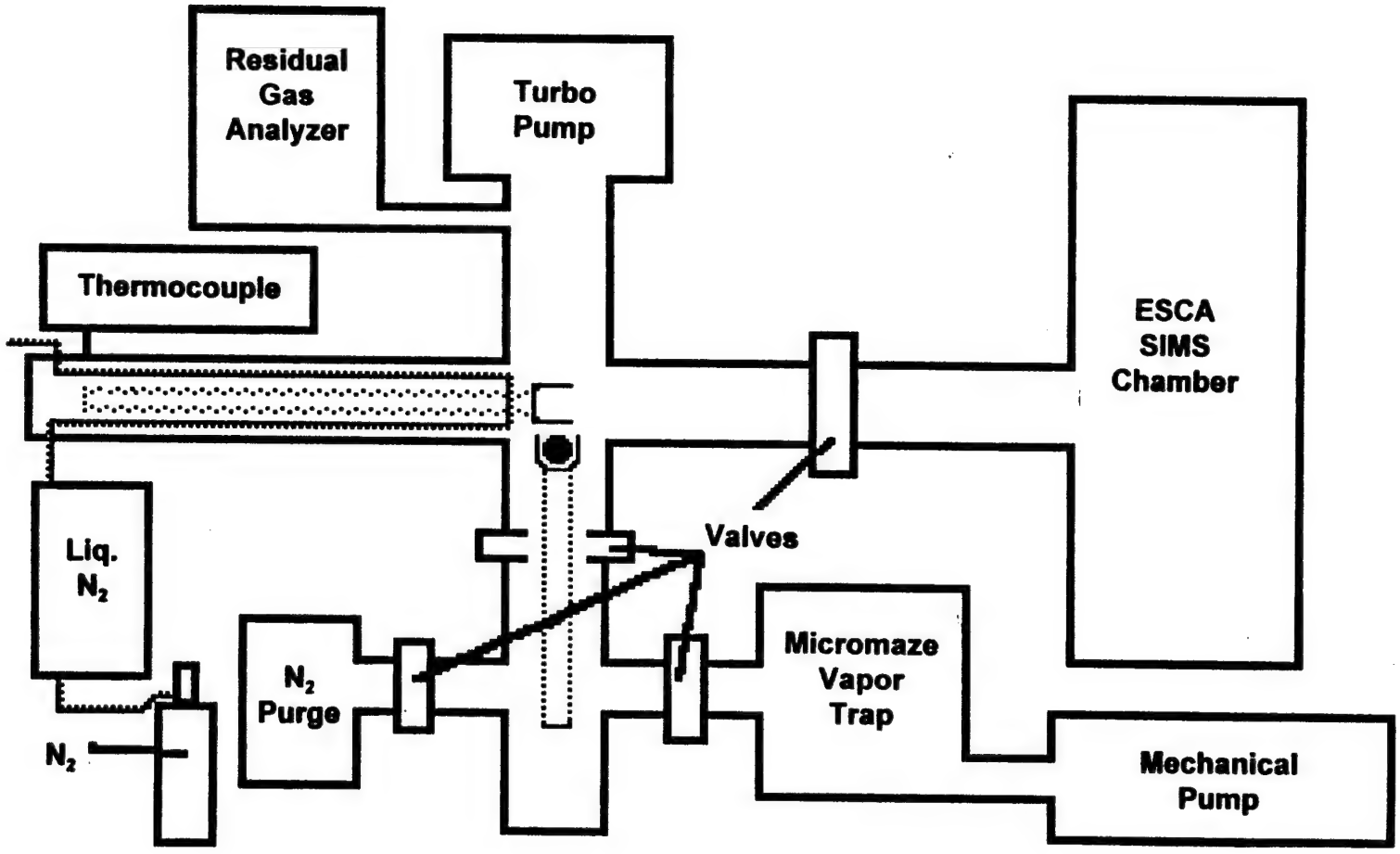
Turbo Pump
ESCA SIMS Chamber
Thermocouple
Valves
Liq. N_2
N_2 Purge
Micromaze Vapor Trap
Mechanical Pump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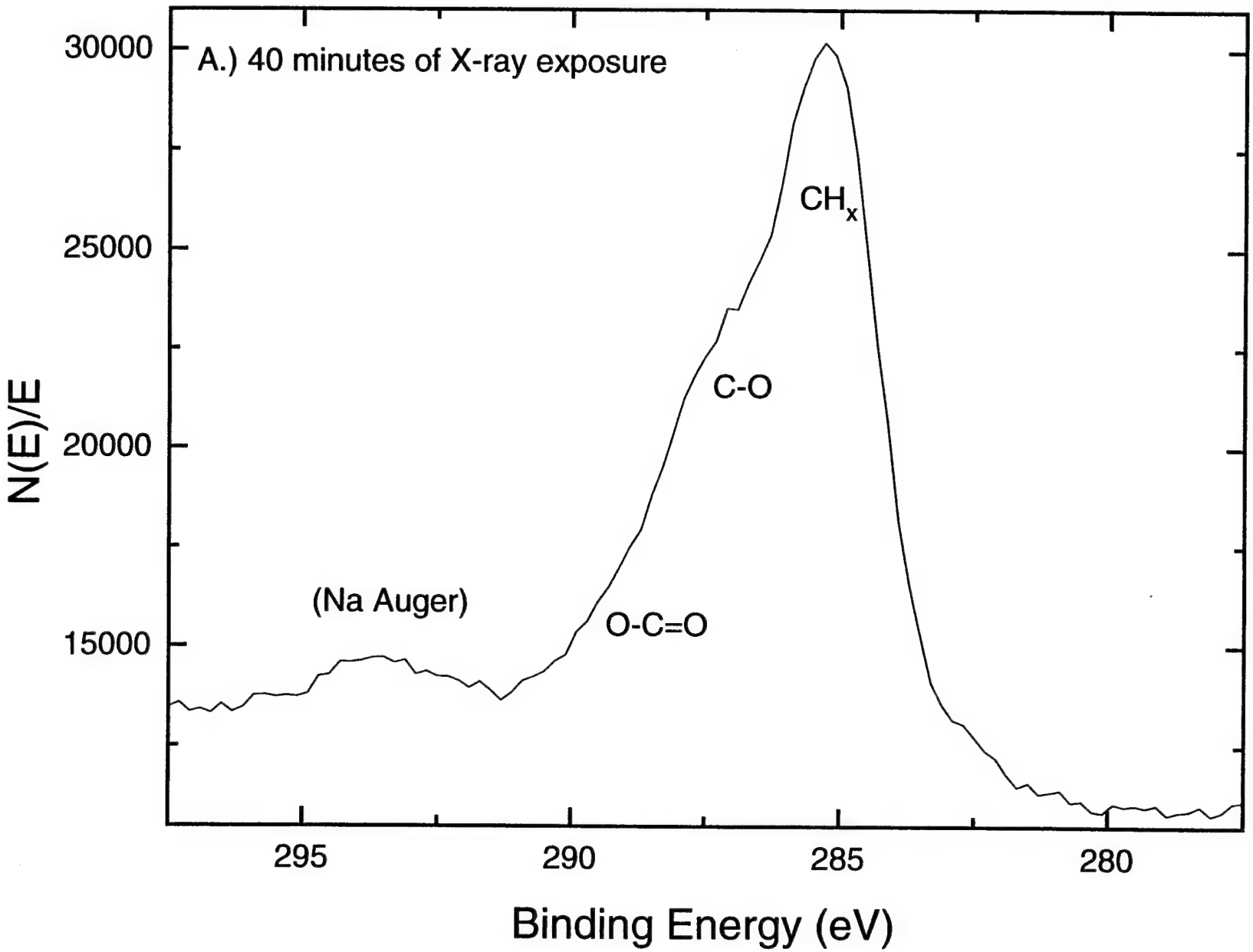
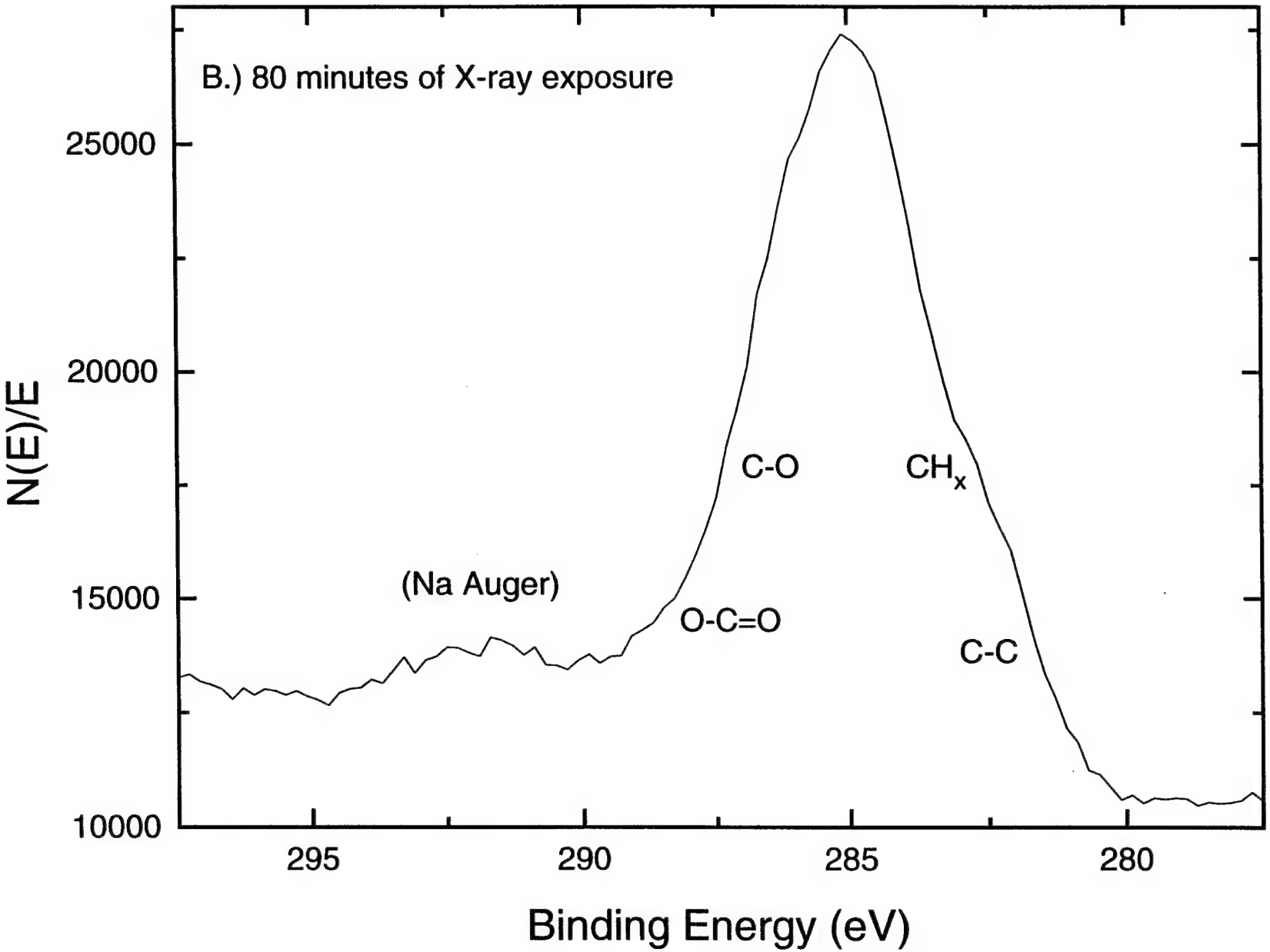
Vapor
Trap
N_2
Mechanical
Pump


A.) 40 minutes of X-ray exposure
30000
25000
20000
15000
N(E)/E
CH$_x$
C-O
O-C=O
(Na Auger)
295
290
285
280
Binding Energy (eV)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20000
15000
10000
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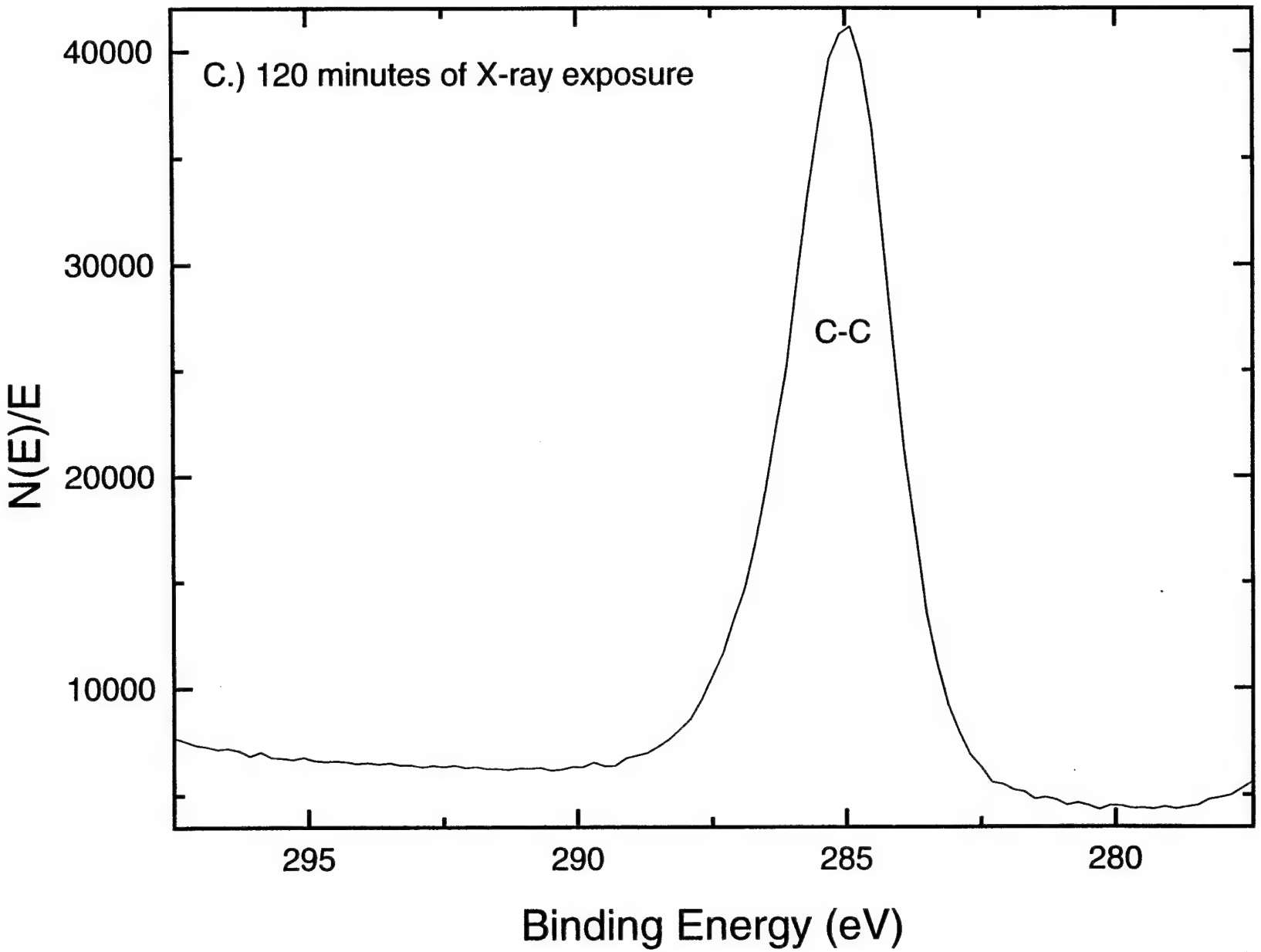
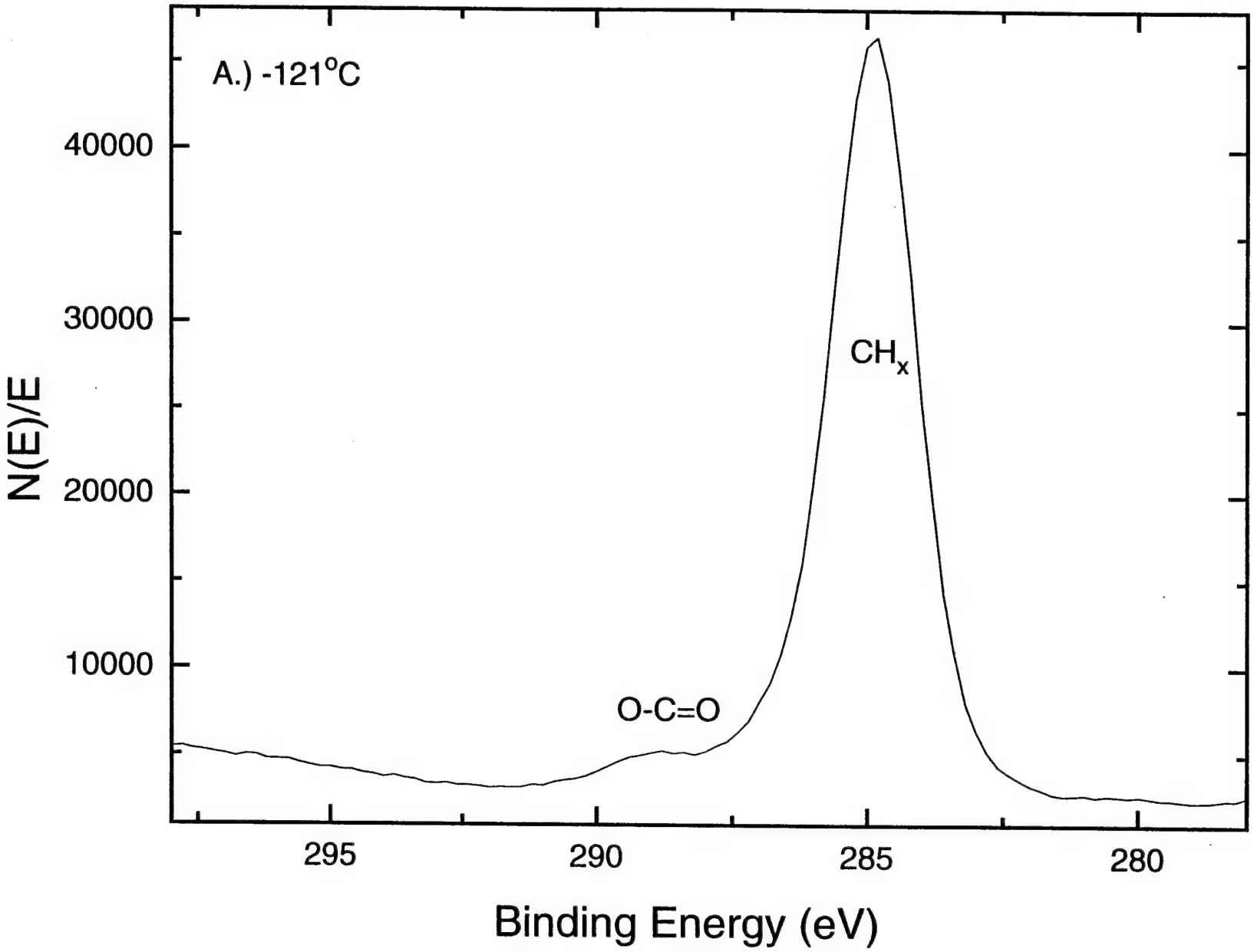
C-O
CHx
(Na Auger)
O-C=O
C-C
295
290
285
280
Binding Energy (eV)


C.) 120 minutes of X-ray exposure
C-C
40000
30000
20000
10000
N(E)/E
295
290
285
280
Binding Energy (eV)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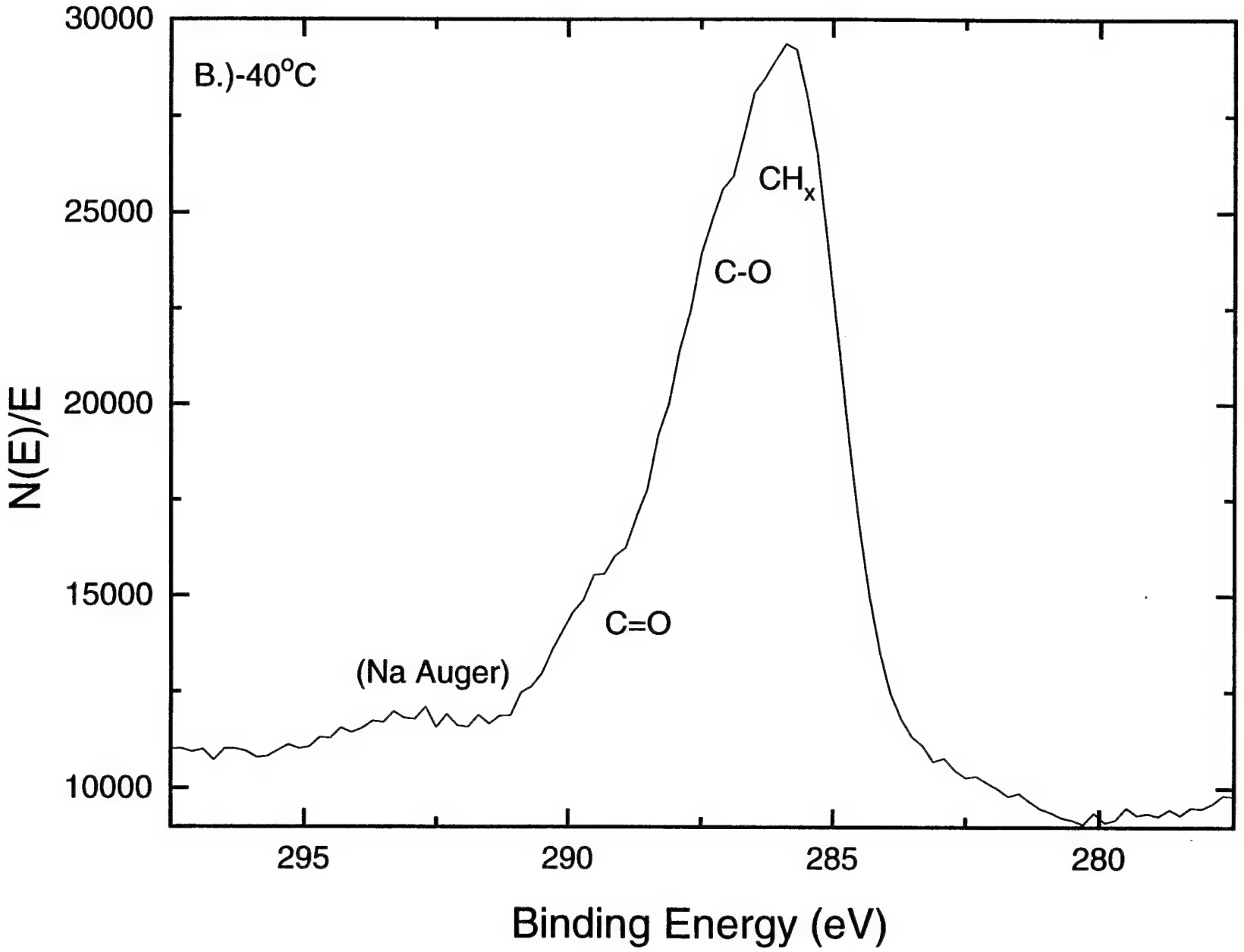
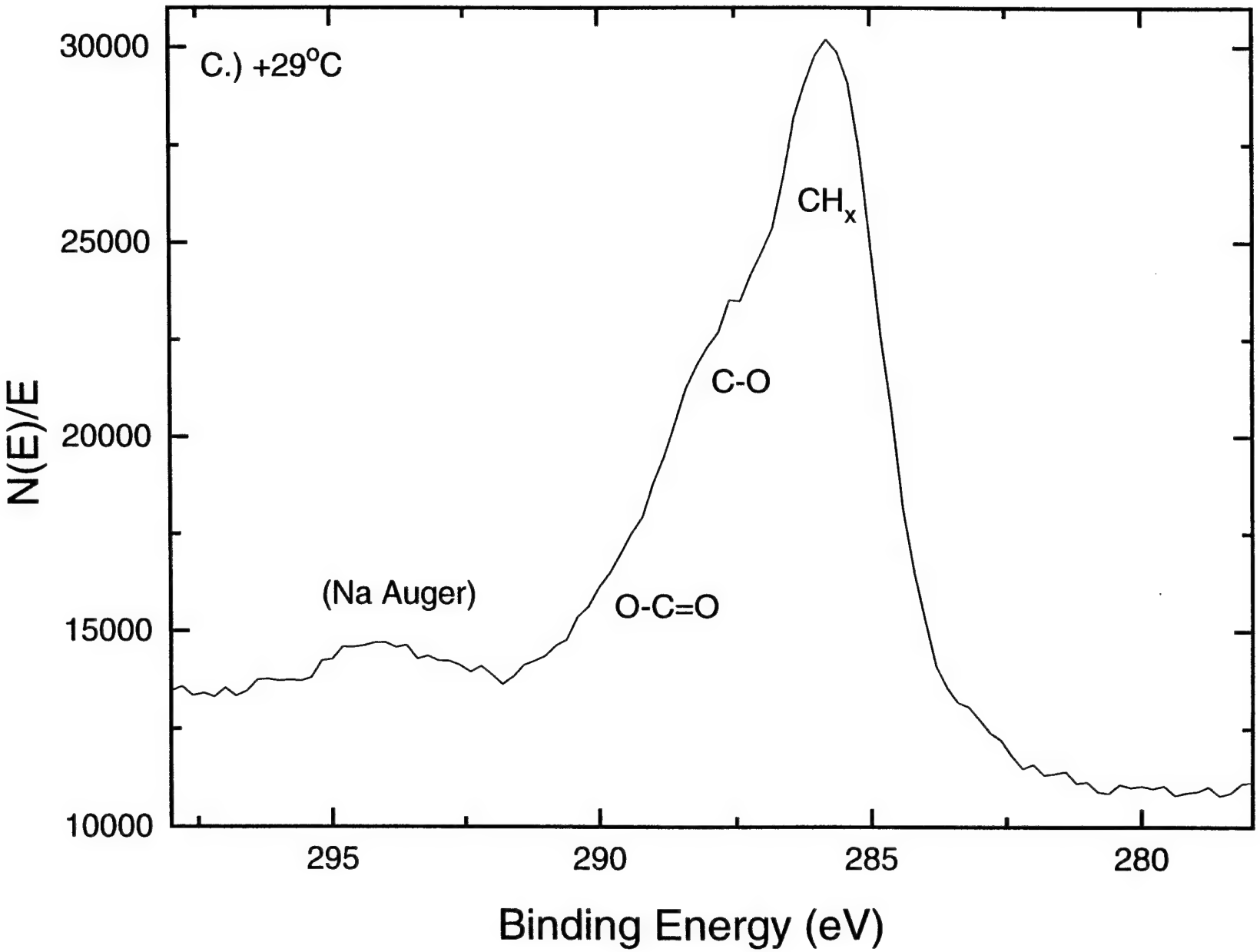
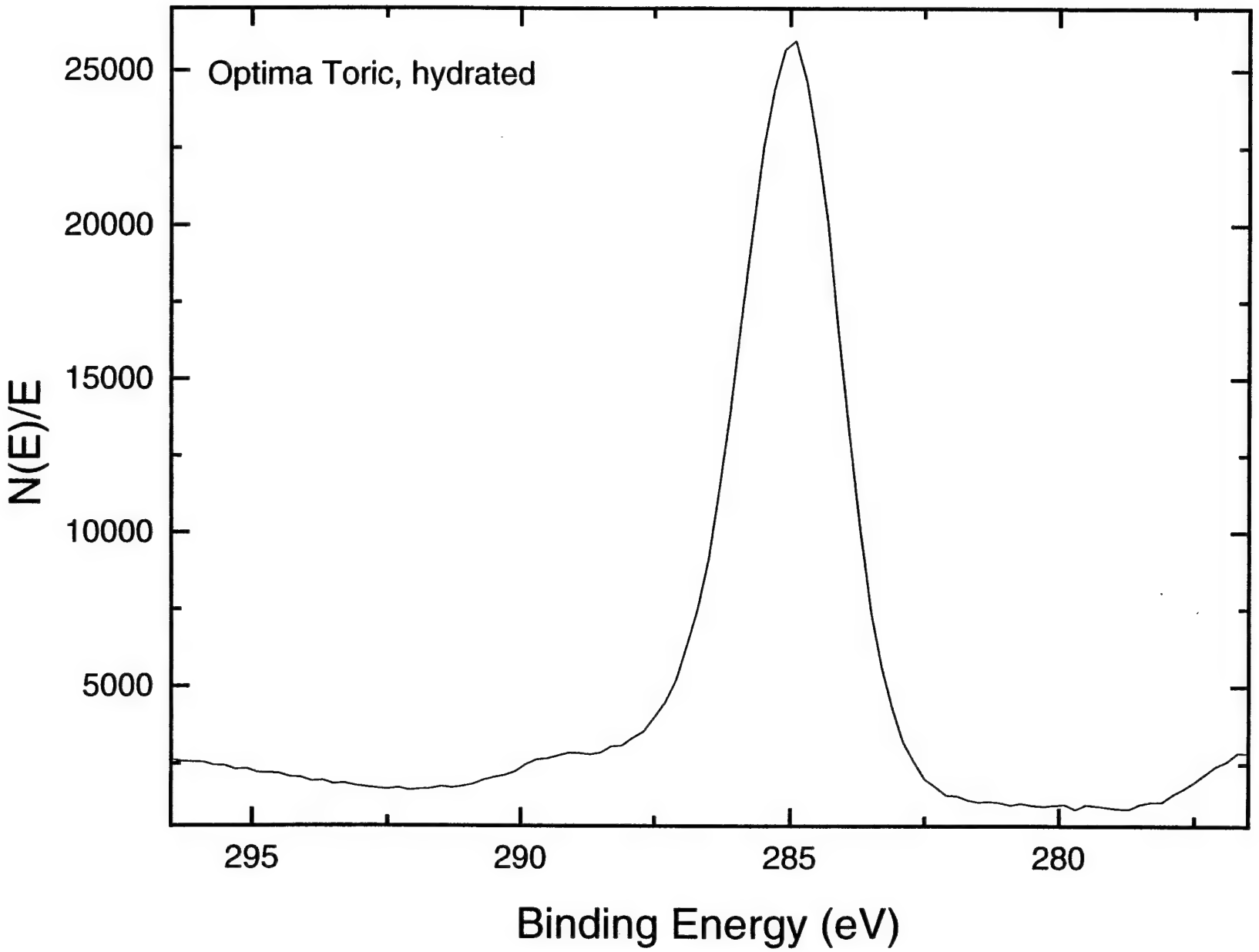
30000
20000
10000
N(E)/E
CHx
O-C=O
295
290
285
280
Binding Energy (eV)


B.)-40°C
CH$_x$
C-O
C=O
(Na Auger)
30000
25000
20000
15000
10000
N(E)/E
295
290
285
280
Binding Energy (eV)


C.) +29°C
30000
25000
20000
15000
10000
N(E)/E
295
290
285
280
Binding Energy (eV)
CH$_x$
C-O
O-C=O
(Na Auger)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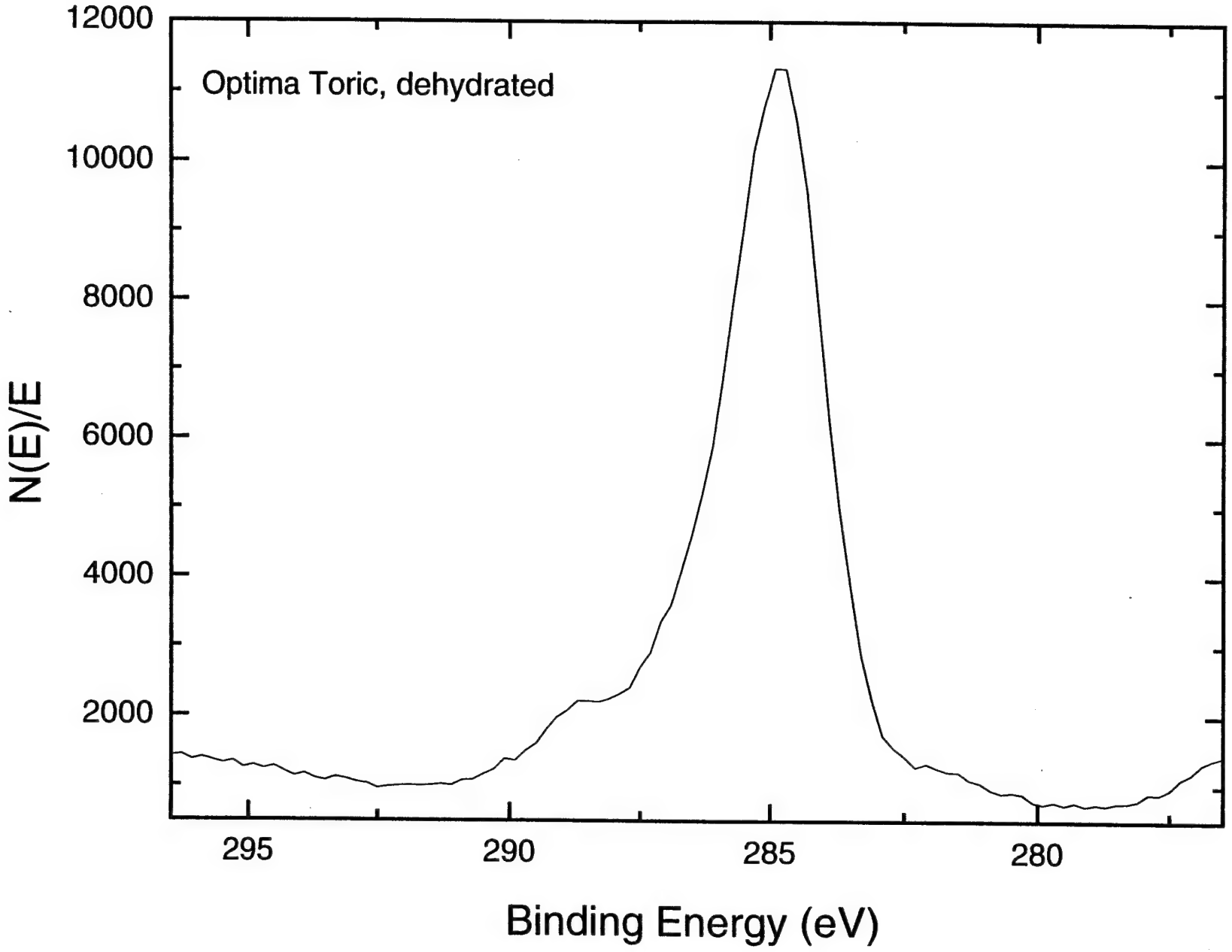
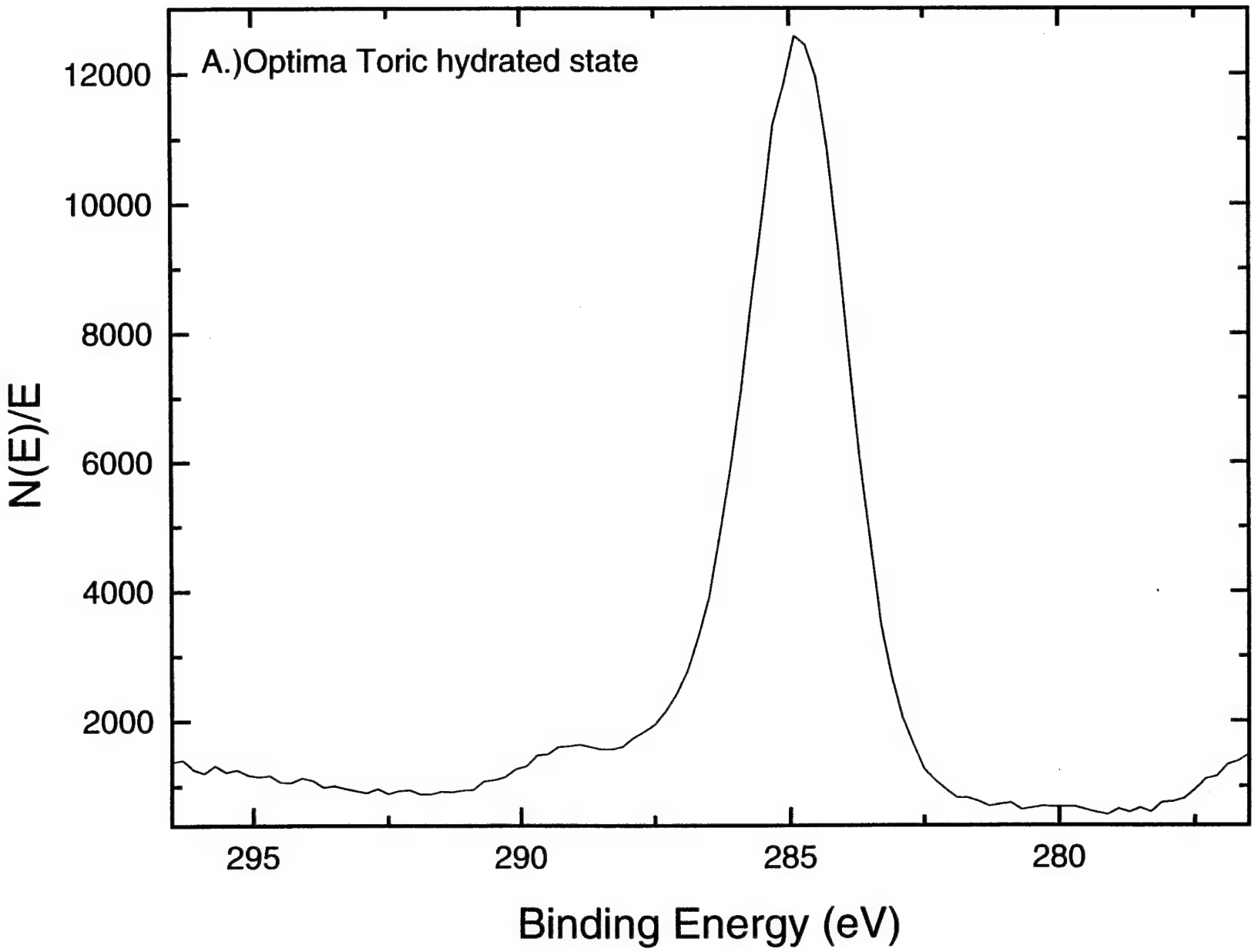
25000
20000
15000
10000
5000
N(E)/E
295
290
285
280
Binding Energy (eV)


Optima Toric, dehydrated
12000
10000
8000
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)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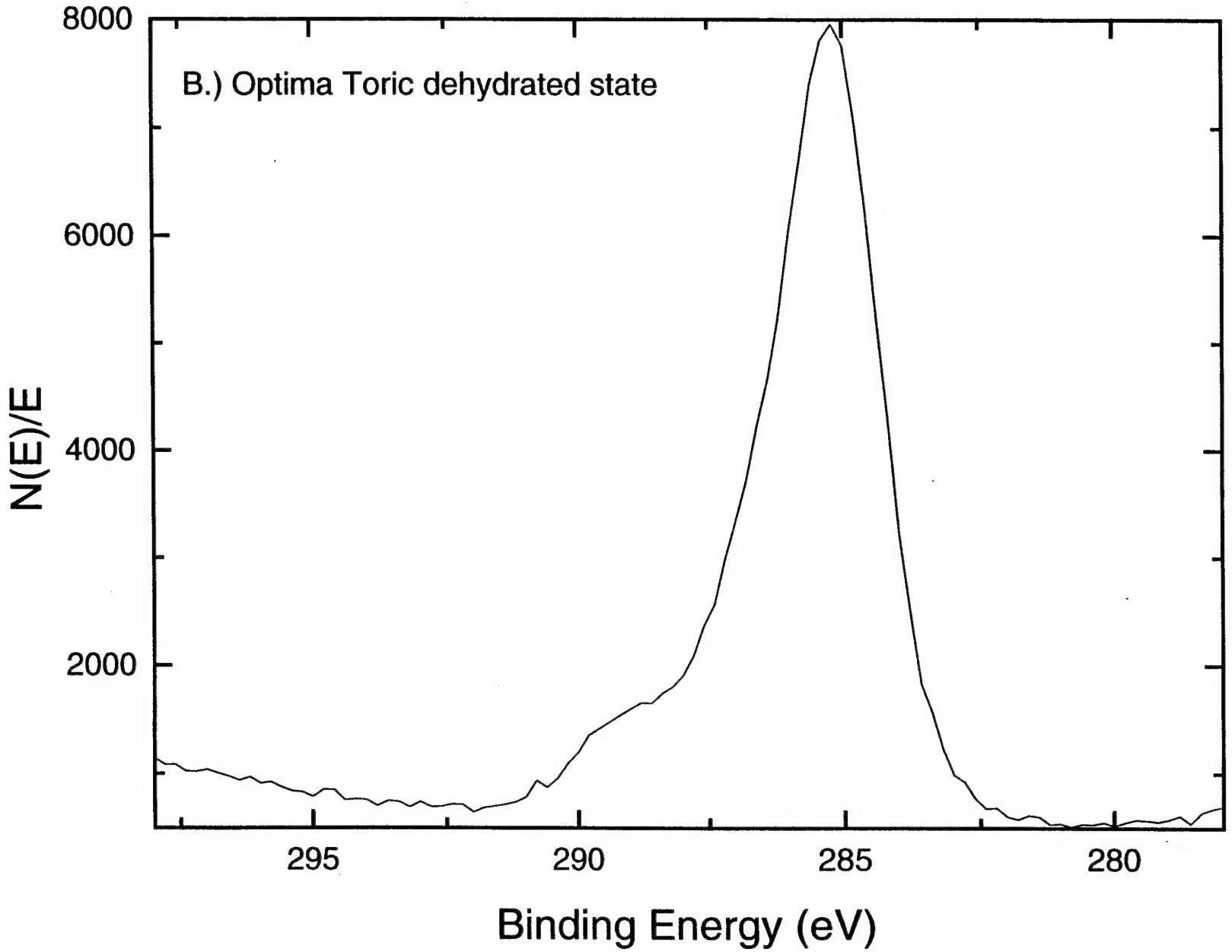
12000
10000
8000
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)


B.) Optima Toric dehydrated state
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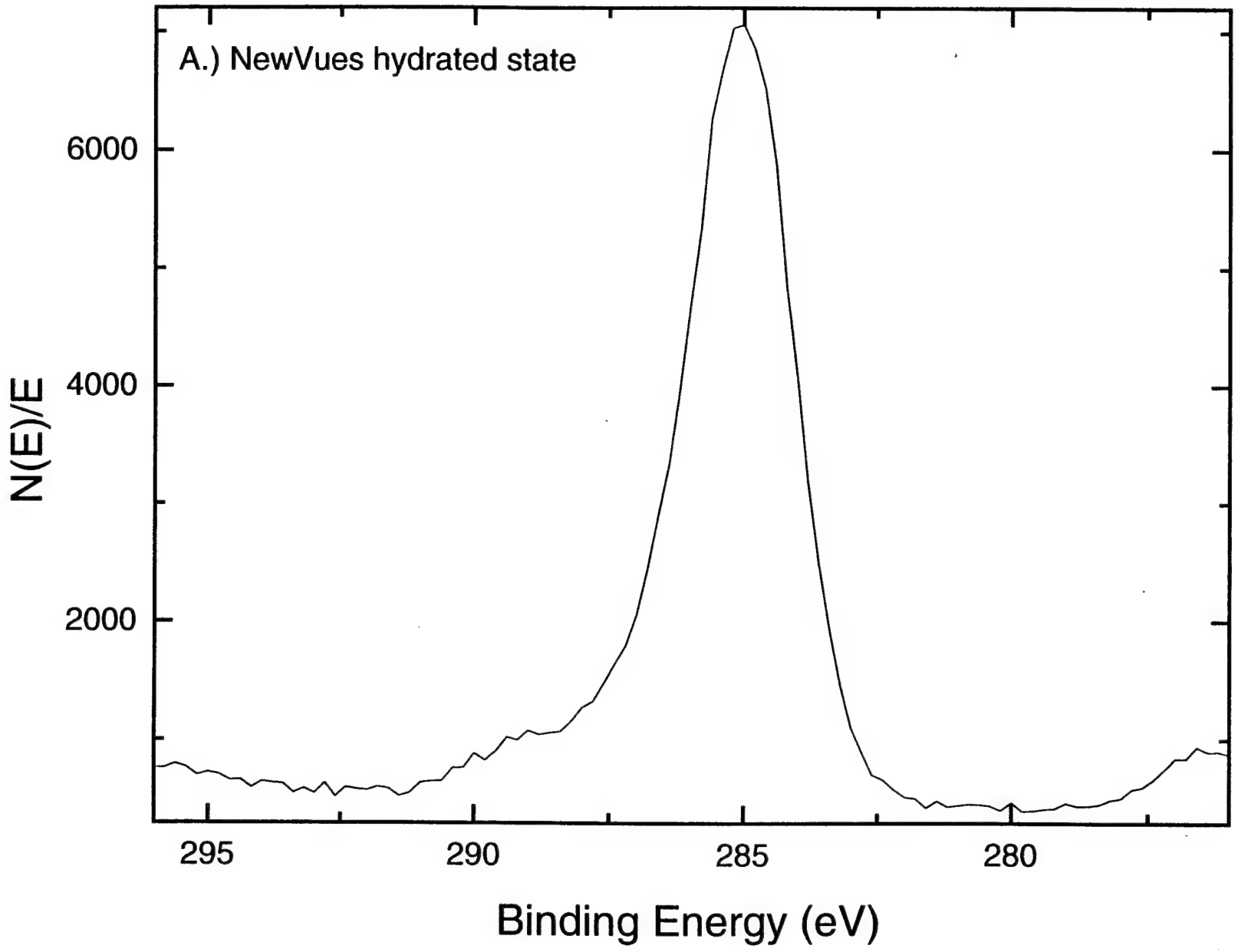
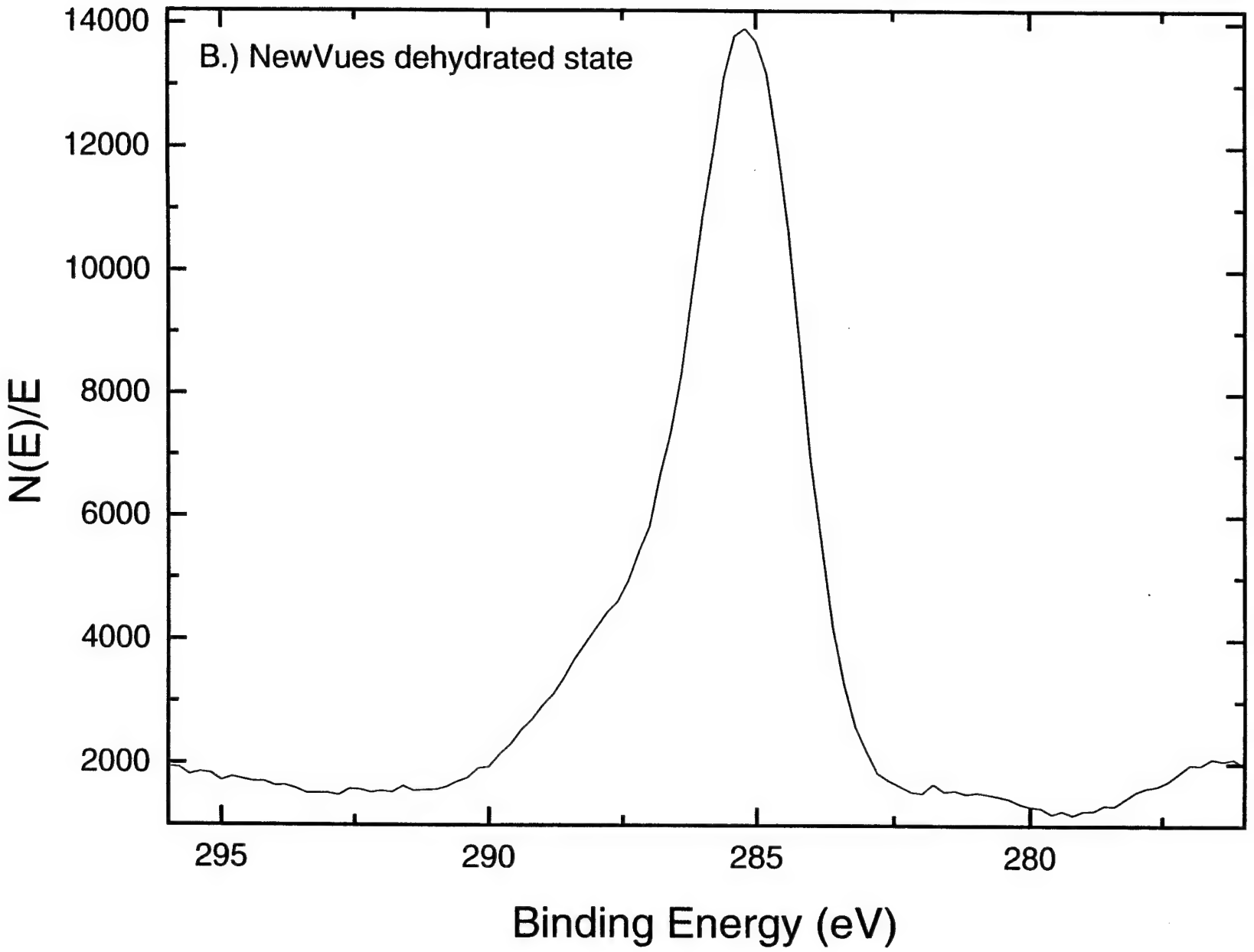
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)


A.) NewVues hydrated state
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)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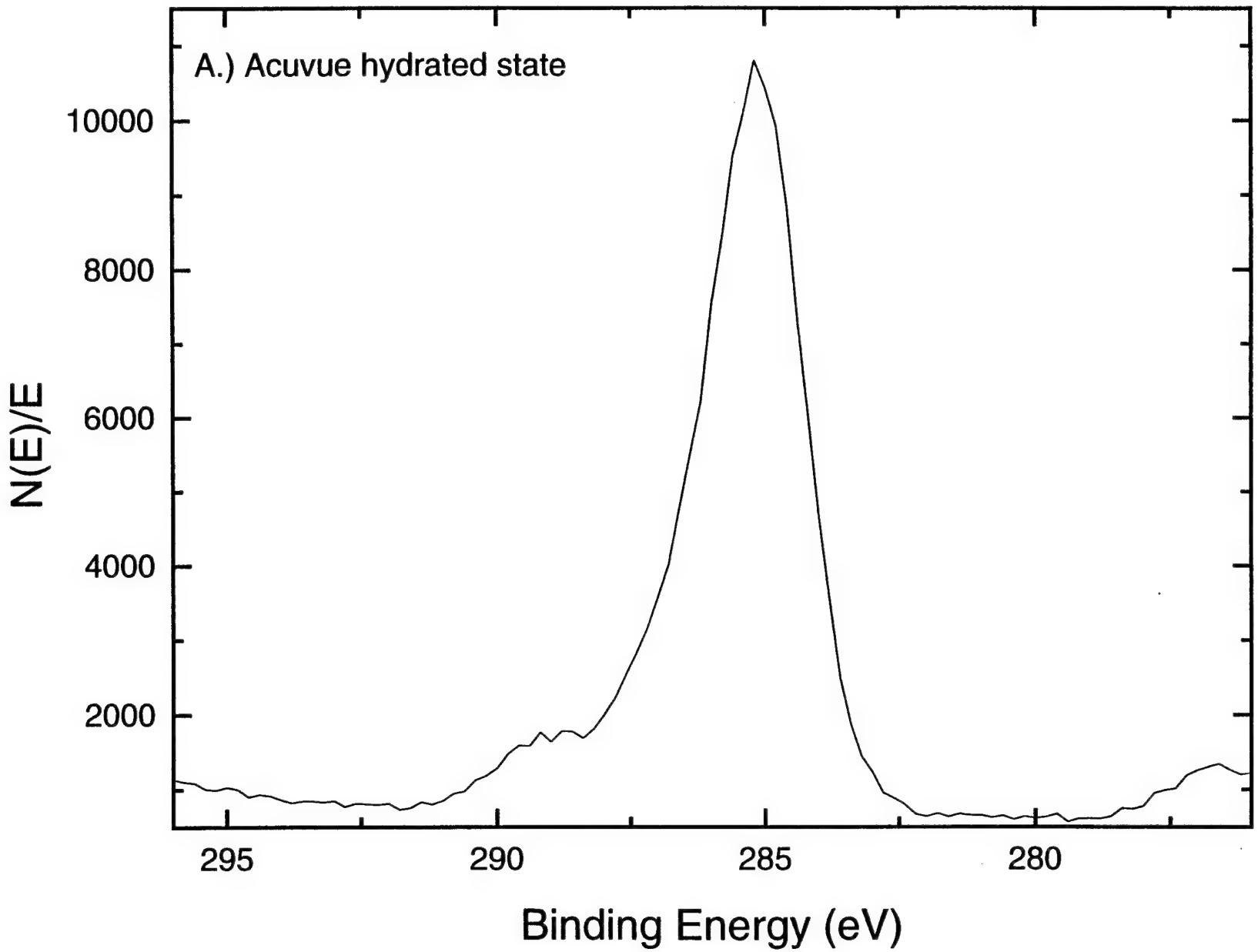
14000
12000
10000
8000
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)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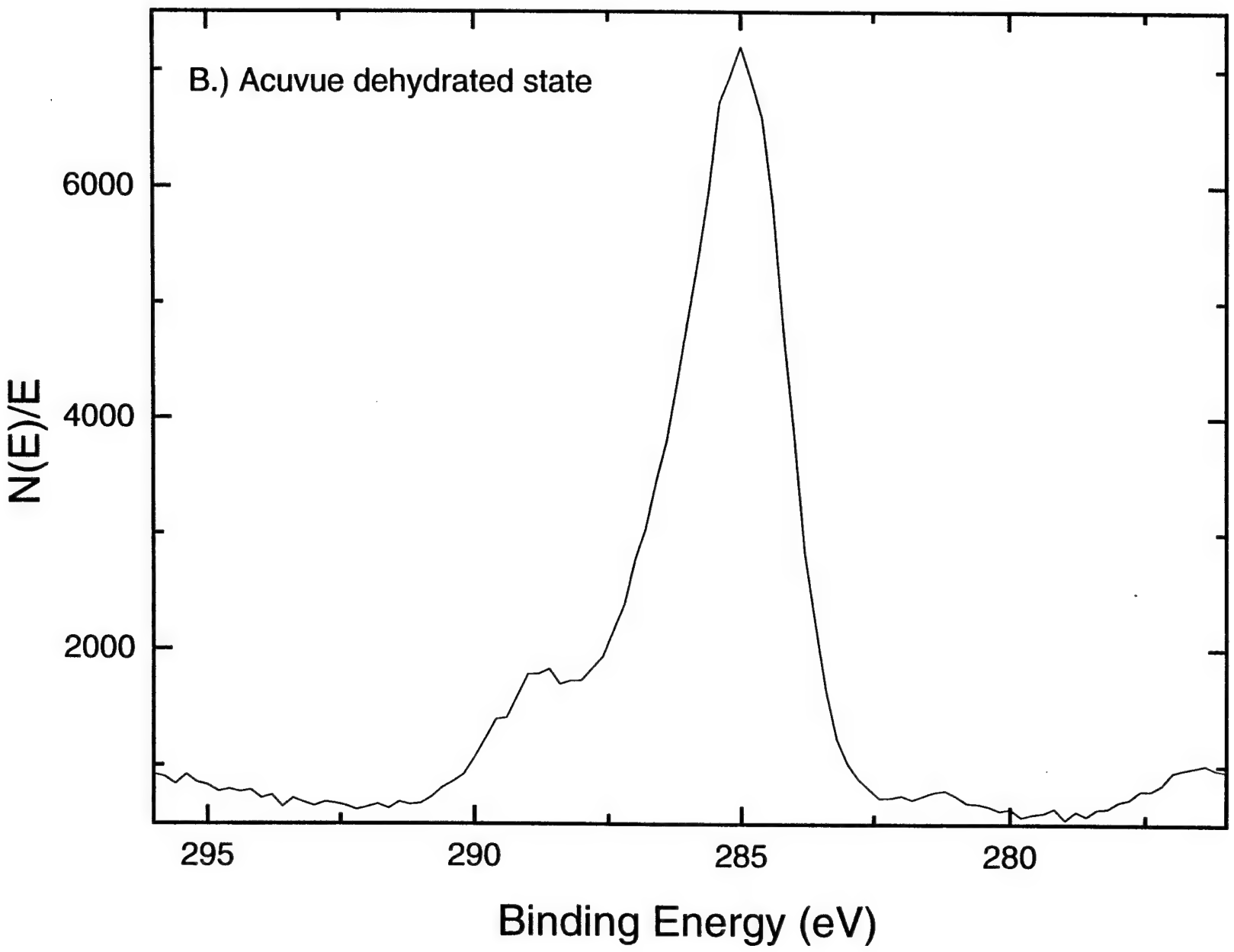
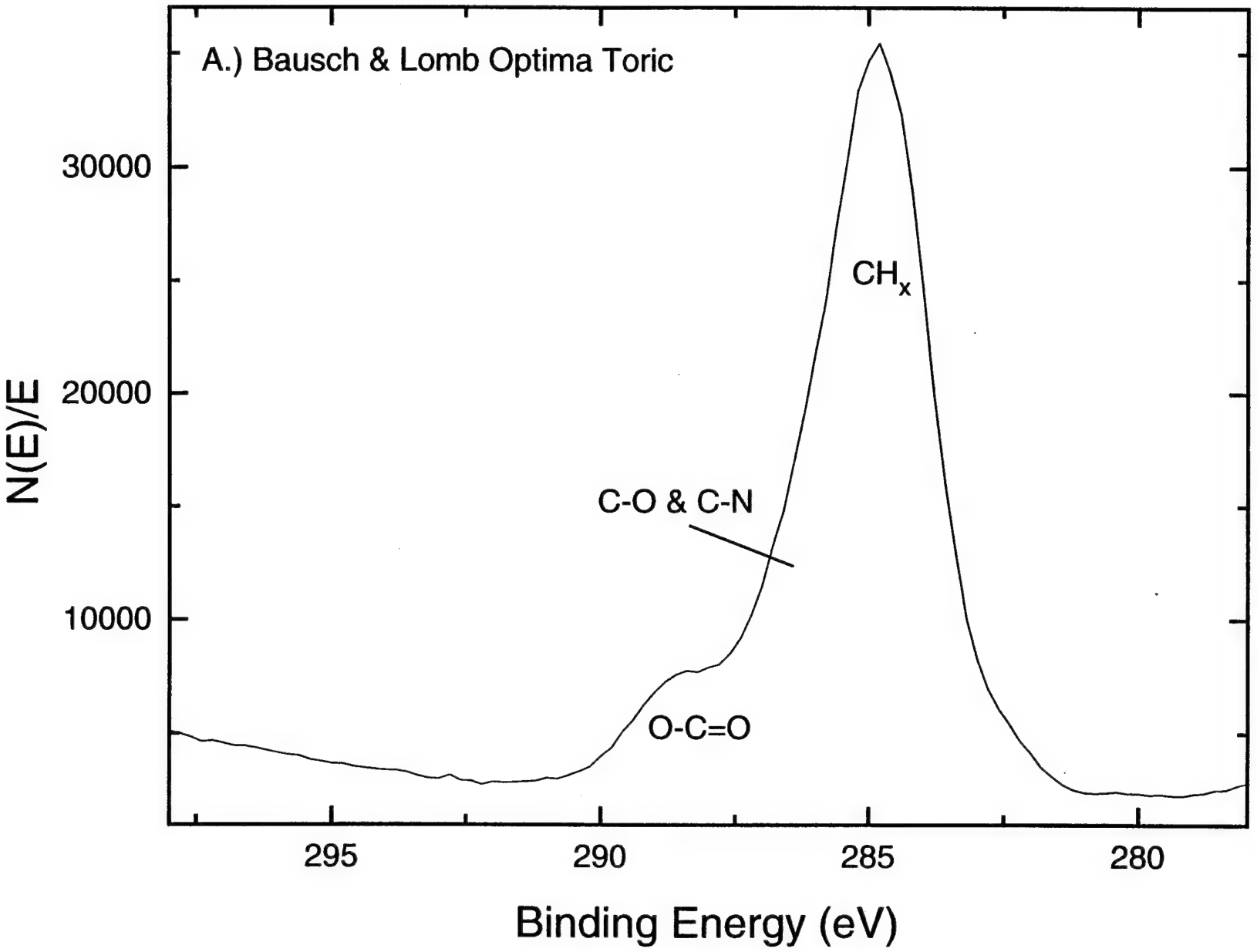
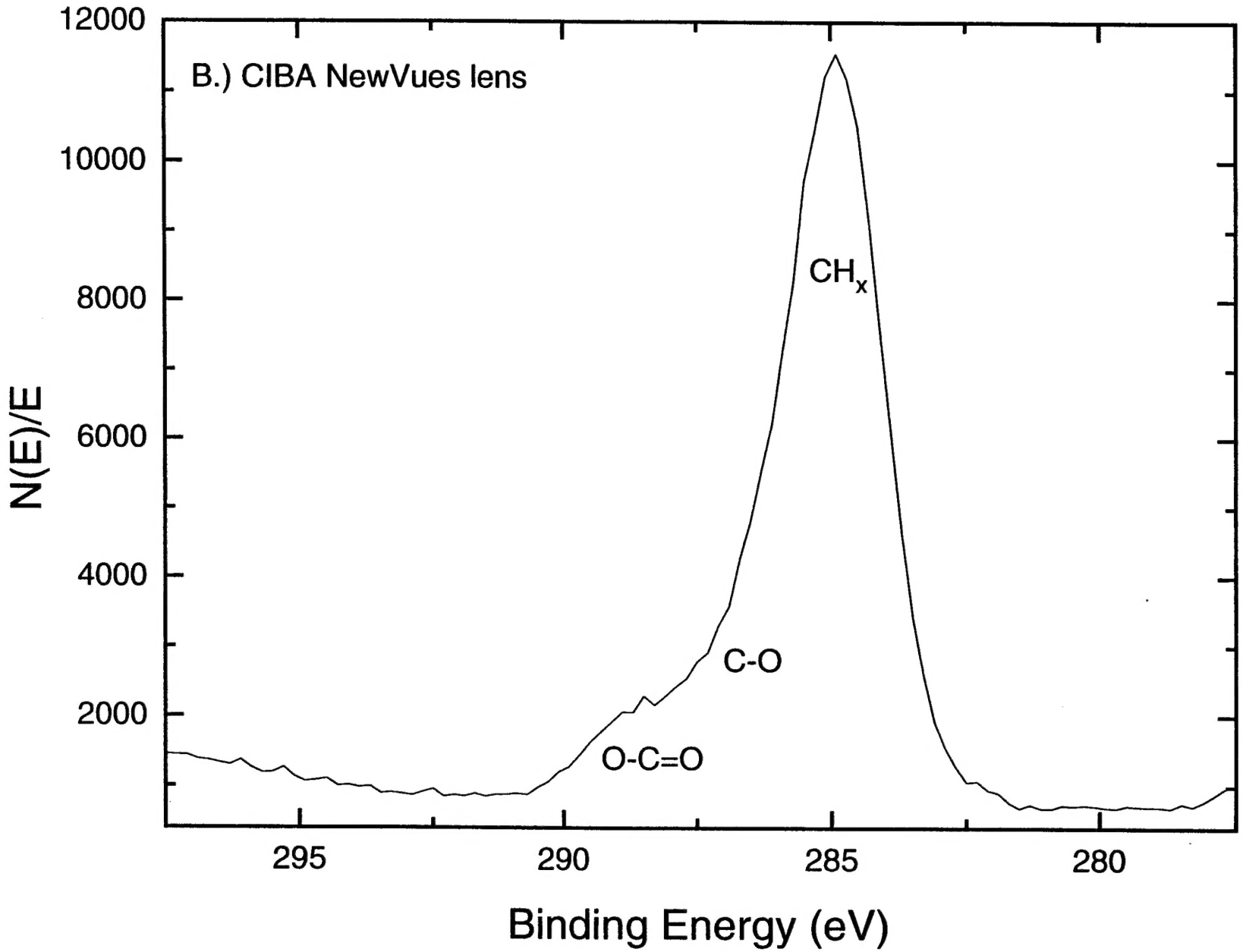
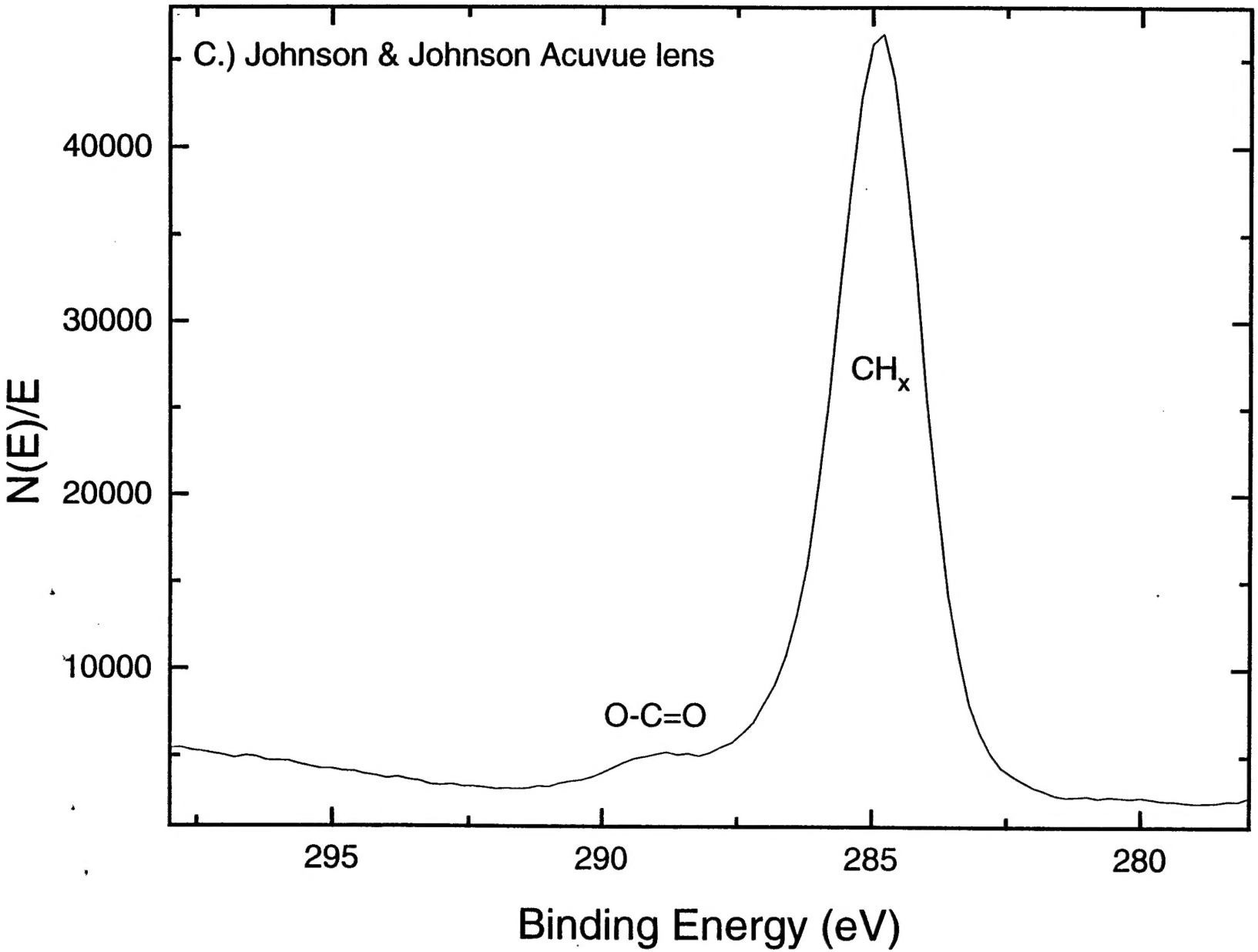
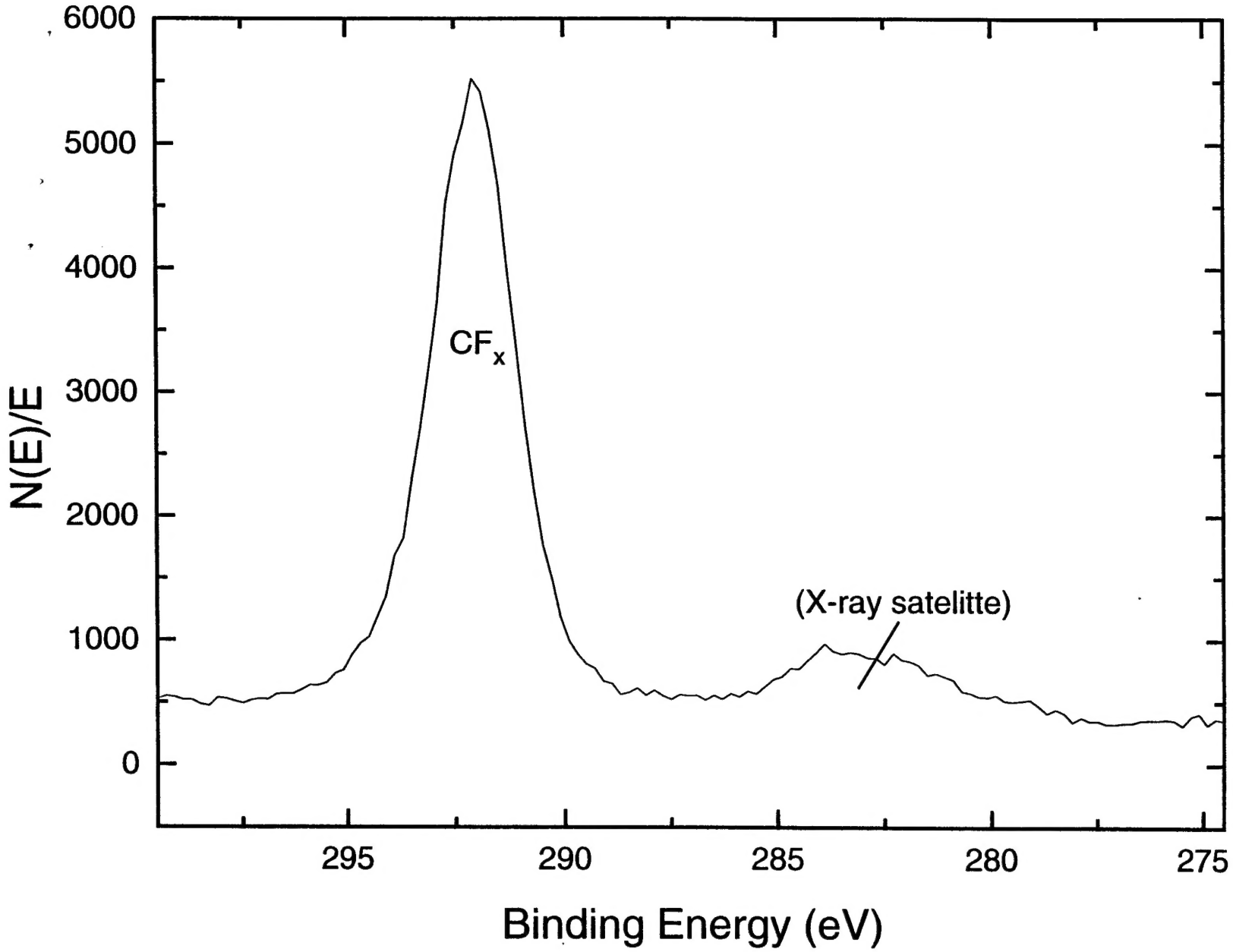
10000
8000
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)


B.) Acuvue dehydrated state
6000
4000
2000
N(E)/E
295
290
285
280
Binding Energy (eV)


A.) Bausch & Lomb Optima Toric
30000
20000
10000
N(E)/E
CH$_x$
C-O & C-N
O-C=O
295
290
285
280
Binding Energy (eV)


B.) CIBA NewVues lens
12000
10000
8000
6000
4000
2000
N(E)/E
CH$_x$
C-O
O-C=O
295
290
285
280
Binding Energy (eV)


C.) Johnson & Johnson Acuvue lens
40000
30000
20000
10000
N(E)/E
CHx
O-C=O
295
290
285
280
Binding Energy (eV)


6000
5000
4000
3000
2000
1000
0
N(E)/E
CF$_x$
(X-ray satelitte)
295
290
285
280
275
Binding Energy (eV)

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